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A Concise Course on the Theory of Classical Liquids

Basics and Selected Topics

Springer

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To Ángeles, María del Mar, and David

Foreword

I have been fortunate to have lived through a period during which the theory of liquids passed from being considered to be one of the unsolved problems in physics to a solved, even mature, field. When I was a student, it was felt that the gas and solid phases were understood, but the lack of a theory of liquids was believed to be a gap in our understanding of nature. I was attracted by this perceived gap and wished to play a role in changing this. In retrospect, it is amusing that an almost satisfactory theory, the van der Waals theory, was available but unappreciated. A half century ago, this theory was regarded as being of only pedagogic interest. In this theory, the contributions of the repulsive and attractive forces are treated by two separate terms. The repulsive forces in this theory are described in terms of hard-sphere interactions. Even though it was clear from the beginning that the treatment of the hard-sphere forces in the van der Waals theory, through a simple free volume, $V - Nb$, was inadequate, this was ignored and attention was directed, almost exclusively, to making empirical changes in the form of the term representing the attractive forces. Various modifications, not based on theory, were proposed on a "try this, try that" basis in order to give a more accurate value for pV/NkT at the critical point. This was misguided; it is now known that the critical point cannot be described adequately by any analytic equation. Indeed, the theory of the critical point is now regarded as a separate field. In contrast, the van der Waals treatment of the attractive forces is well founded. It is the treatment of the repulsive forces in terms of a simple free volume that is the major problem in the original form of van der Waals theory. Even though it was clear to van der Waals and his contemporaries that his expression for the free volume is a poor, even bad, approximation that grossly overestimated the hard-sphere pressure, it was retained in the various modifications that were considered. It was the treatment of the attractive forces that drew attention. The reason for retaining the free volume term of van der Waals was that only a cubic equation needs to be solved to give the volume in terms of the pressure. This, certainly, was a convenience in the days before electronic computers and avoided an iterative solution. However, from the point of view of the development of liquid state theory, it was a case of putting the cart before the horse. It is now clear that it was the nature of the gas phase at high densities, rather than the liquid phase, that was poorly understood. It was the gas phase at high densities, in particular the equation of state of the hard-sphere fluid, that was the unsolved problem. Computer simulation of hard spheres and the analytic solution of the Percus–Yevick equation for hard-spheres provided an understanding of the hard sphere gas and changed everything.

Professor Santos has presented a comprehensive treatment of liquid state theory with a clear development of integral equation theory, including the Percus–Yevick theory and the closely related hypernetted-chain and mean spherical theories. The discussion of the hard-sphere fluid is, appropriately, generous. One notable, and desirable feature of his book is the collection of photographs of some of the notables in the development of liquid state theory. Nonscientists tend to think of science as an impersonable field with scientists working in isolation. In reality, science is quite sociable with scientists interacting with each other and being stimulated through this interaction. This sociable interaction in agreeable locations is one reason that schools, such as the Warsaw schools, are so valuable and enjoyable. The large, impersonable meetings of scientific societies have their place, but, generally, it is at small meetings and schools that the real progress is made.

I look forward to placing Professor Santos' book on my bookshelf as a valuable reference and am confident that many of our peers will do this also. I am grateful to Professor Santos for writing this valuable book and for giving me the opportunity to play a small part in its production.

Provo, UT, USA
November 2015

Douglas Henderson

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.

Badajoz, Spain
December 2015

Andrés Santos

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First, I want to express my gratitude to those scientists with whom I have had the privilege to collaborate in problems related to equilibrium statistical mechanics of classical fluids over the years. They are, in alphabetical order, Luis Acedo, Morad Alawneh, Mariana Bárcenas, Elena Beltrán-Heredia, Arieh Ben-Naim, J. Javier Brey, Francisco Castaño, Riccardo Fantoni, Giacomo Fiumara, Achille Giacometti, Douglas Henderson, Julio Largo, Mariano López de Haro, Stefan Luding, Miguel Ángel G. Maestre, Alexandr Malijevský, Anatol Malijevský, Gema Manzano, Gerardo Odriozola, Vitaliy Ogarko, Pedro Orea, Jarosław Piasecki, Miguel Robles, René D. Rohrmann, Francisco Romero, Luis F. Rull, Franz Saija, J. Ramón Solana, Carlos F. Tejero, and Santos B. Yuste.

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I am very grateful as well to Christian Caron, Executive Publishing Editor of Physics at Springer, who first suggested the possibility of expanding my original Warsaw lecture notes into this book and who very kindly accepted my frequent requests for deadline extensions. Suresh Kumar, from TeX Support Team of SPi Content Solutions–SPi Global, was extremely quick and efficient in helping me with some latex technical questions.

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Last, but certainly not least, let me thank my wife Angeles for her continuous support and encouragement and for patiently putting up with my "Penelope-like" tendency to re-elaborate previous (and supposedly finished) parts of the text.

Contents

Acronyms

The number between parentheses refers to the page where the acronym is first introduced.

AHS	Additive hard spheres (p. 39)
BGHLL	Boublík–Grundke–Henderson–Lee–Levesque (p. 224)
BMCSL	Boublík–Mansoori–Carnahan–Starling–Leland (p. 224)
BS	Barrio–Solana (p. 79)
CS	Carnahan–Starling (p. 76)
DCF	Direct correlation function (p. 105)
EoS	Equation of state (p. 39)
GMSA	Generalized mean spherical approximation (p. 240)
H	Henderson (p. 72)
HD	Hard disk (p. 72)
HNC	Hypernetted-chain (p. 176)
HR	Hard rod (p. 146)
HS	Hard sphere (p. 37)
L	Luding (p. 74)
LDH	Linearized Debye–Hückel (p. 182)
LJ	Lennard-Jones (p. 37)
MC	Monte Carlo (p. 58)
MD	Molecular dynamics (p. 72)
MSA	Mean spherical approximation (p. 182)
NAHR	Nonadditive hard rods (p. 146)
NAHS	Nonadditive hard spheres (p. 39)
OZ	Ornstein–Zernike (p. 105)
PS	Penetrable sphere (p. 37)
PSW	Penetrable square well (p. 89)
PY	Percus–Yevick (p. 176)
RDF	Radial distribution function (p. 101)
RFA	Rational-function approximation (p. 204)
SHR	Sticky hard rod (p. 141)

SHS	Sticky hard sphere (p. 38)
SHY	Santos–Haro–Yuste (p. 74)
SPT	Scaled particle theory (p. 75)
SS	Square shoulder (p. 37)
SW	Square well (p. 37)
SYH	Santos–Yuste–Haro (p. 78)
vdW	van der Waals (p. 78)

Symbols

The number between parentheses refers to the page where the symbol is first introduced.

a	Helmholtz free energy per particle (p. 10)
a^{ex}	Excess Helmholtz free energy per particle (p. 79)
$a^{\mathrm{ex}}_{\mathrm{oc}}$	Excess Helmholtz free energy per particle of the one-component fluid (p. 79)
A_j	Numerical coefficients in $\mathfrak{R}(q)$ (p. 71)
$\mathscr{A}$	Auxiliary function related to a^{ex} (p. 82)
$\mathscr{A}_0$	Auxiliary function related to $\mathscr{A}$ (p. 83)
b_k	Rescaled virial coefficient of a hard-sphere fluid (p. 54)
$\hat{b}_k$	Rescaled virial coefficient of a hard-sphere mixture (p. 79)
$b_{k_1;k-k_1}$	Rescaled composition-independent virial coefficient in a binary AHS mixture (p. 52)
$\mathfrak{b}_\ell$	Cluster integral (p. 41)
B_k	Virial coefficient (p. 40)
$\widehat{B}_{k_1;k-k_1}$	Composition-independent virial coefficient in a binary mixture (p. 52)
$\widehat{B}_{\nu_1\nu_2\cdots\nu_k}$	Composition-independent virial coefficient in a mixture (p. 50)
$\widehat{B}^{(\mathrm{I,II,III})}_{\alpha\gamma\delta\varepsilon}$	Partial contributions to the composition-independent virial coefficient $\widehat{B}_{\alpha\gamma\delta\varepsilon}$ (p. 51)
$\mathrm{B}(a,b)$	Beta function (p. 58)
$\mathrm{B}_x(a,b)$	Incomplete beta function (p. 58)
$\mathscr{B}(r)$	"Bridge" (or "elementary") diagrams (p. 171)
$c(r)$	Direct correlation function (p. 105)
$\tilde{c}(k)$	Fourier transform of $c(r)$ (p. 106)
$c_{\alpha\gamma}(r)$	Direct correlation function in a mixture (p. 117)
$\tilde{c}_{\alpha\gamma}(k)$	Fourier transform of $c_{\alpha\gamma}(r)$ (p. 118)
$\check{\mathsf{c}}(k)$	Matrix with elements $n\sqrt{x_\alpha x_\gamma}\tilde{c}_{\alpha\gamma}(k)$ (p. 118)
C_j	Numerical coefficients in $\mathfrak{R}(q)$ (p. 71)
C_p	Heat capacity at constant pressure (p. 6)
C_V	Heat capacity at constant volume (p. 6)

c_N	Quantum of phase-space volume (p. 15)
$\mathscr{C}(r)$	"Chains" (or nodal diagrams) (p. 170)
d	Dimensionality of the system (p. 13)
$\widehat{D}(s)$	Determinant of the matrix $\delta_{\alpha\gamma} - \widehat{Q}_{\alpha\gamma}(s)$ (p. 133)
$\mathrm{D}_a(z)$	Parabolic cylinder function (p. 56)
$e(r)$	Pair Boltzmann factor (p. 177)
E	Internal energy (p. 1)
$\widetilde{E}$	Most probable value of the energy in a closed system (p. 19)
$\langle E\rangle^{\mathrm{ex}}$	Excess average energy (p. 28)
$\langle E\rangle^{\mathrm{id}}$	Average energy of the ideal gas (p. 26)
$f(r)$	Mayer function (p. 34)
f_{ij}	Mayer function evaluated at $r = r_{ij}$ (p. 42)
$f_{\alpha\gamma}(r)$	Mayer function for a pair of species α and γ (p. 39)
$\tilde{f}_{\alpha\gamma}(k)$	Fourier transform of $f_{\alpha\gamma}(r)$ (p. 64)
$f_s(\mathbf{x}^s)$	s-body reduced distribution function (p. 97)
F	Helmholtz free energy (p. 4)
F^{ex}	Excess Helmholtz free energy (p. 28)
F^{id}	Helmholtz free energy of the ideal gas (p. 26)
$\widehat{F}(s)$	Auxiliary function related to the Laplace transform $\widehat{G}(s)$ (p. 207)
$g(r)$	Radial distribution function (p. 101)
$g_{\alpha\gamma}(r)$	Radial distribution function in a mixture (p. 116)
$g_s(\mathbf{r}^s)$	s-body correlation function (p. 100)
G	Gibbs free energy (p. 5)
G^{id}	Gibbs free energy of the ideal gas (p. 26)
$\widehat{G}(s)$	Laplace transform representation of $g(r)$ (pp. 127, 204, and 205)
$\widehat{G}_{\alpha\gamma}(s)$	Laplace transform representation of $g_{\alpha\gamma}(r)$ (pp. 205 and 218)
h	Planck constant (p. 15)
$h(r)$	Total correlation function (p. 102)
$h_{\alpha\gamma}(r)$	Total correlation function in a mixture (p. 117)
$h_s(\mathbf{r}^s)$	s-body cluster correlation function (p. 100)
$\tilde{h}(k)$	Fourier transform of $h(r)$ (p. 103)
$\tilde{h}_{\alpha\gamma}(k)$	Fourier transform of $h_{\alpha\gamma}(r)$ (p. 117)
$\check{\mathsf{h}}(k)$	Matrix with elements $n\sqrt{x_\alpha x_\gamma}\tilde{h}_{\alpha\gamma}(k)$ (p. 118)
H	Enthalpy (p. 11)
$\widehat{H}(s)$	Laplace transform representation of $h(r)$ (pp. 131 and 205)
$\widehat{H}_{\alpha\gamma}(s)$	Laplace transform representation of $h_{\alpha\gamma}(r)$ (p. 218)
$H_N(\mathbf{x}^N)$	Hamiltonian of a one-component system (p. 13)
$H_N^{\mathrm{id}}(\mathbf{p}^N)$	Hamiltonian of the ideal gas (p. 26)
$H_{\{N_\nu\}}(\mathbf{x}^N)$	Hamiltonian of a mixture (p. 29)
I	Identity matrix (p. 118)
$\mathrm{I}_x(a,b)$	Regularized beta function (p. 58)
$j_k(x)$	Spherical Bessel function (p. 205)
$J_\nu(x)$	Bessel function (p. 64)
$\widehat{J}$	Auxiliary quantity in one-dimensional mixtures (p. 134)

k	Wave number (p. 64)
k_B	Boltzmann constant (p. 10)
K	Normalization constant in $p^{(1)}(r)$ (p. 132)
$K_{\alpha\gamma}$	Normalization constant in $p_{\alpha\gamma}^{(1)}(r)$ (p. 128)
$\mathscr{K}_x^{(k)}$	kth cumulant of a random variable x (p. 19)
L	Length of a one-dimensional system (p. 125)
$L^{(k)}$	Parameters in the solution of the Percus–Yevick equation for hard spheres (p. 209) and in the rational-function approximation for hard spheres (p. 238) and square-well fluids (p. 241)
$\bar{L}^{(k)}$	Parameters in the rational-function approximation for square-well fluids (p. 241)
$\mathscr{L}$	Laplace transform (p. 205)
$\mathscr{L}^{-1}$	Inverse Laplace transform (p. 137)
m	Mass of a particle (p. 26)
m_k	Reduced kth moment of the size distribution in a hard-sphere mixture (p. 79)
M_k	kth moment of the size distribution in a hard-sphere mixture (p. 63)
n	Total number density (p. 2)
$n_s(\mathbf{r}^s)$	s-body configurational distribution function (p. 98)
n_s^{id}	s-body configurational distribution function of the ideal gas (p. 100)
n^*	Reduced number density (pp. 103 and 136)
n_ν	Number density of species ν (p. 2)
$n_{\alpha\gamma}$	Pair configurational distribution function in a mixture (p. 115)
N	Total number of particles (p. 1)
N_ν	Number of particles of species ν (p. 1)
$\widetilde{N}$	Most probable value of the number of particles in an open system (p. 22)
p	Pressure (p. 2)
p^{ex}	Excess pressure (p. 28)
p^{id}	Pressure of the ideal gas (p. 26)
$p^{(\ell)}(r)$	ℓth neighbor distribution function (p. 126)
$p_{\alpha\gamma}^{(\ell)}(r)$	ℓth neighbor distribution function in a mixture (p. 131)
$\mathbf{p}_i$	Momentum vector of particle i (p. 13)
$\mathbf{p}^N$	Set of N momentum vectors (p. 13)
$\widehat{P}^{(\ell)}(s)$	Laplace transform of $p^{(\ell)}(r)$ (p. 126)
$\widehat{P}_{\alpha\gamma}^{(\ell)}(s)$	Laplace transform of $p_{\alpha\gamma}^{(\ell)}(r)$ (p. 132)
$\widehat{\mathsf{P}}^{(1)}(s)$	Matrix of elements $\widehat{P}_{\alpha\gamma}^{(1)}(s)$ (p. 132)
$\mathscr{P}(r)$	Open "parallel" diagrams (or open "bundles") (p. 171)
$\mathscr{P}^{+}(r)$	"Parallel" diagrams (or "bundles") (p. 172)
$\mathscr{P}(N)$	Number probability distribution function in the grand canonical ensemble (p. 22)
$\mathscr{P}^{\mathrm{id}}(N)$	Number probability distribution function of the ideal gas in the grand canonical ensemble (p. 31)

$\mathscr{P}_N(E)$	Energy probability distribution function in the canonical ensemble (p. 19)
$\mathscr{P}_N^{\mathrm{id}}(E)$	Energy probability distribution function of the ideal gas in the canonical ensemble (p. 31)
$\mathscr{P}_N(V)$	Volume probability distribution function in the isothermal–isobaric ensemble (p. 24)
$\mathscr{P}_N^{\mathrm{id}}(V)$	Volume probability distribution function of the ideal gas in the isothermal–isobaric ensemble (p. 31)
q	Size ratio (p. 70)
q_0	Special value of the size ratio (p. 69)
$\widehat{Q}(s)$	Auxiliary functions related to $\widehat{P}^{(1)}_{\alpha\gamma}(s)$ (p. 133)
$\mathscr{Q}_N$	Configuration integral (p. 27)
$\mathscr{Q}_{\{N_\nu\}}$	Configuration integral of a mixture (p. 92)
r_0	Location of the minimum of the interaction potential (p. 56)
r_0^*	Location of the minimum of the interaction potential in reduced units (p. 57)
r_{ij}	Distance between the centers of particles i and j (p. 33)
$\mathbf{r}_i$	Position vector of particle i (p. 13)
$\mathbf{r}^N$	Set of N position vectors (p. 13)
R	Auxiliary quantity in one-dimensional mixtures (p. 133)
$\mathfrak{R}(q)$	Auxiliary function in $b_{2;2}(q)$ (p. 71)
s	Parameter of the generalized Lennard-Jones potential (p. 56)
S	Entropy (p. 1)
S^{id}	Entropy of the ideal gas (p. 26)
$\widetilde{S}(k)$	Structure factor (p. 103)
$\widetilde{S}_{\alpha\gamma}(k)$	Structure factor in a mixture (p. 117)
$\widetilde{\mathsf{S}}(k)$	Matrix with elements $\widetilde{S}_{\alpha\gamma}(k)$ (p. 118)
$S^{(k)}$	Parameters in the solution of the Percus–Yevick equation for hard spheres (p. 209) and in the rational-function approximation for hard spheres (p. 238) and square-well fluids (p. 241)
$\mathscr{S}[\rho_N]$	Gibbs entropy functional (p. 15)
T	Temperature (p. 2)
T^*	Reduced temperature (p. 55)
T_B	Boyle temperature (p. 57)
T_B^*	Reduced Boyle temperature (p. 57)
u	Internal energy per particle (p. 10)
u^{ex}	Excess internal energy per particle (p. 112)
$u_{\mathrm{ext}}(\mathbf{r})$	External potential (p. 158)
U_ℓ	Cluster function (p. 44)
v_d	Volume of a d-dimensional sphere of unit diameter (p. 53)
V	Volume (p. 1)
$\widetilde{V}$	Most probable value of the volume in the isothermal–isobaric system (p. 25)
V_0	Arbitrary volume scale factor (p. 15)

$\mathscr{V}_{a,b}(r)$	Intersection volume of two spheres of radii a and b whose centers are separated a distance r (p. 65)
$\bar{\mathscr{V}}_{a,b}(r)$	Relevant part of $\mathscr{V}_{a,b}(r)$ (p. 65)
w	Auxiliary function in the Percus–Yevick solution for sticky hard spheres (p. 227)
$w(r)$	Shifted cavity function (p. 183)
$\widetilde{w}(k)$	Fourier transform of $w(r)$ (p. 183)
W_N	N-body functions in the expansion of Ξ in powers of fugacity (p. 42)
x_ν	Mole fraction of species ν (p. 1)
$x(\sigma)$	Continuous size distribution in a polydisperse hard-sphere system (p. 87)
$\mathbf{x}^N$	Point in the N-body phase space (p. 13)
X	Generic thermodynamic quantity (p. 41)
X_k	Coefficient in the expansion of X in powers of density (p. 41)
$\overline{X}_\ell$	Coefficient in the expansion of X in powers of fugacity (p. 41)
$y(r)$	Cavity function (p. 104)
$y_{\alpha\gamma}(r)$	Cavity function in a mixture (p. 117)
z	Fugacity (p. 17)
$\hat{z}$	Rescaled fugacity (p. 28)
Z	Compressibility factor (p. 10)
Z_{oc}	Compressibility factor of the one-component fluid (p. 78)
$\mathscr{Z}_N$	Partition function (p. 18)
$\mathscr{Z}_N^{\text{id}}$	Partition function of the ideal gas (p. 26)
$\mathscr{Z}_{\{N_\nu\}}$	Partition function of a mixture (p. 29)
α	Opposite of chemical potential divided by thermal energy (p. 17)
α_p	Thermal expansivity (p. 7)
$\alpha_\ell(\mathbf{r}_1, \mathbf{r}_2)$	Coefficients in the expansion of $n_2(\mathbf{r}_1, \mathbf{r}_2)$ in powers of fugacity (p. 163)
β	Inverse temperature parameter (p. 10)
γ	Pressure divided by thermal energy (p. 23)
$\gamma_k(\mathbf{r}_1, \mathbf{r}_2)$	Coefficients in the expansion of $n_2(\mathbf{r}_1, \mathbf{r}_2)$ in powers of density (p. 164)
$\overline{\gamma}(r)$	Indirect correlation function (p. 181)
$\Gamma(x)$	Gamma function (p. 26)
$\delta(x)$	Dirac delta function (p. 16)
Δa^*	Surplus Helmholtz free energy per particle (p. 84)
Δa^*_{oc}	Surplus Helmholtz free energy per particle of the one-component fluid (p. 85)
$\Delta b_{3;1}$	Rescaled partial contribution to $\widehat{B}_{3;1}$ (p. 70)
Δp^*	Surplus pressure (p. 84)
Δp^*_{oc}	Surplus pressure of the one-component fluid (p. 85)
ΔE	Energy tolerance (p. 16)
$\varDelta_N$	Isothermal–isobaric partition function (p. 23)
$\varDelta_N^{\text{id}}$	Isothermal–isobaric partition function of the ideal gas (p. 26)

$\Delta_{\{N_\nu\}}$	Isothermal–isobaric partition function of a mixture (p. 29)
ε	Energy scale of the interaction potential (p. 37)
ζ	One-particle partition function (p. 26)
η	Packing fraction (pp. 54 and 78)
η_{cp}	Close-packing value of η (p. 74)
$\theta(\mathbf{r})$	Boltzmann factor associated with the external potential $u(\mathbf{r})$ (p. 158)
$\theta_k(x)$	Reverse Bessel polynomials (p. 205)
$\Theta(x)$	Heaviside step function (p. 38)
ϑ_i	Species of particle i (p. 115)
κ_T	Isothermal compressibility (p. 7)
Λ	Thermal de Broglie wavelength (p. 27)
Λ_α	Thermal de Broglie wavelength in a mixture (p. 30)
$\Lambda^{(k)}$	Parameters in the solution of the Percus–Yevick equation for hard spheres (p. 209) and sticky hard spheres (p. 225)
$\Lambda_{\alpha\gamma}(s)$	Auxiliary functions in the solution of the Percus–Yevick equation for sticky-hard-sphere mixtures (p. 220)
$\Lambda_{\alpha\gamma}^{(k)}$	Parameters in the solution of the Percus–Yevick equation for sticky-hard-sphere mixtures (p. 220)
μ	Chemical potential (p. 9)
$\overline{\mu}$	Species-averaged chemical potential (p. 5)
μ^{ex}	Excess chemical potential (p. 28)
μ^{id}	Chemical potential of the ideal gas (p. 26)
μ_ν	Chemical potential of species ν (p. 2)
μ_ν^{ex}	Excess chemical potential of species ν (p. 119)
ξ	Coupling parameter (p. 110)
Ξ	Grand partition function (p. 20)
Ξ^{id}	Grand partition function of the ideal gas (p. 26)
ϖ_k	Parameter defined as a combination of moments of the size distribution (p. 82)
$\Pi_{a,b}(x)$	Boxcar function (p. 16)
$\rho_N(\mathbf{x}^N)$	Phase-space probability density (p. 14)
$\rho_{\{N_\nu\}}(\mathbf{x}^N)$	Phase-space probability density of a mixture (p. 29)
σ	Length scale of the interaction potential (p. 37)
σ_α	Diameter of a sphere of species α (p. 39)
$\sigma_{\alpha\gamma}$	Closest distance between two spheres of species α and γ (p. 39)
$\varsigma_\eta, \varsigma_p$	Parameters combining the second and third virial coefficients of a hard-sphere mixture (p. 84)
$\Sigma_{\alpha\gamma}(s)$	Auxiliary functions in the solution of the Percus–Yevick equation for sticky-hard-sphere mixtures (p. 220)
$\overline{\Sigma}_{\alpha\gamma}$	Parameters in the solution of the Percus–Yevick equation for sticky-hard-sphere mixtures (p. 221)
τ	Inverse stickiness parameter (p. 38)
$\tau_{\alpha\gamma}$	Inverse stickiness parameter in a mixture (p. 219)
$\widehat{\Upsilon}$	Laplace transform of $\phi(r)e^{-\beta\phi(r)}$ (p. 130)

$\phi(r)$	Interaction potential (p. 33)
$\phi^*(r^*)$	Reduced interaction potential (p. 57)
$\phi_{\alpha\gamma}(r)$	Interaction potential for a pair of species α and γ (p. 39)
$\Phi_N(\mathbf{r}^N)$	Total potential energy (p. 27)
$\Phi_{\{N_\nu\}}(\mathbf{r}^N)$	Total potential energy of a mixture (p. 115)
$\varphi_k(x)$	Auxiliary mathematical function (p. 210)
χ_T	Isothermal susceptibility (p. 10)
$\chi_{T,k}$	Coefficient in the expansion of χ_T in powers of density (p. 185)
$\psi(r)$	Potential of mean force (p. 165)
$\Psi_\ell(r)$	Partial contribution to $g(r)$ in the one-dimensional sticky-hard-rod fluid (p. 145)
$\overline{\Psi}_\ell(r)$	Partial contribution to $g(r)$ in the three-dimensional hard-sphere and square-well fluids (p. 207)
$\Psi_\ell^{(j)}(r)$	Partial contribution to $g(r)$ in the one-dimensional square-well fluid (p. 137)
$\Psi_\ell^{(j_1,j_2)}(r)$	Partial contribution to $g_{\alpha\gamma}(r)$ in the one-dimensional nonadditive hard-rod fluid mixture (p. 151)
$\omega_{\Delta E}$	Microcanonical partition function (p. 16)
$\omega_{\Delta E}^{\text{id}}$	Microcanonical partition function of the ideal gas (p. 26)
Ω	Grand potential (p. 6)
Ω^{id}	Grand potential of the ideal gas (p. 26)
$\widehat{\Omega}(s)$	Laplace transform of $e^{-\beta\phi(r)}$ (p. 129)
$\widehat{\Omega}_{\alpha\gamma}(s)$	Laplace transform of $e^{-\beta_{\alpha\gamma}\phi(r)}$ (p. 132)
$\langle\cdots\rangle$	Statistical ensemble average (p. 14)

List of Photographs

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