

*Perturbation Theories for the  
Thermodynamic Properties  
of Fluids and Solids*

*J. R. Solana*



CRC Press  
Taylor & Francis Group

# *Perturbation Theories for the Thermodynamic Properties of Fluids and Solids*

*J. R. Solana*



**CRC Press**

Taylor & Francis Group

Boca Raton London New York

---

CRC Press is an imprint of the  
Taylor & Francis Group, an Informa business

CRC Press  
Taylor & Francis Group  
6000 Broken Sound Parkway NW, Suite 300  
Boca Raton, FL 33487-2742

© 2013 by Taylor & Francis Group, LLC  
CRC Press is an imprint of Taylor & Francis Group, an Informa business

No claim to original U.S. Government works

Printed on acid-free paper  
Version Date: 20130129

International Standard Book Number-13: 978-1-4398-0775-0 (Hardback)

This book contains information obtained from authentic and highly regarded sources. Reasonable efforts have been made to publish reliable data and information, but the author and publisher cannot assume responsibility for the validity of all materials or the consequences of their use. The authors and publishers have attempted to trace the copyright holders of all material reproduced in this publication and apologize to copyright holders if permission to publish in this form has not been obtained. If any copyright material has not been acknowledged please write and let us know so we may rectify in any future reprint.

Except as permitted under U.S. Copyright Law, no part of this book may be reprinted, reproduced, transmitted, or utilized in any form by any electronic, mechanical, or other means, now known or hereafter invented, including photocopying, microfilming, and recording, or in any information storage or retrieval system, without written permission from the publishers.

For permission to photocopy or use material electronically from this work, please access [www.copyright.com](http://www.copyright.com) (<http://www.copyright.com/>) or contact the Copyright Clearance Center, Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923, 978-750-8400. CCC is a not-for-profit organization that provides licenses and registration for a variety of users. For organizations that have been granted a photocopy license by the CCC, a separate system of payment has been arranged.

**Trademark Notice:** Product or corporate names may be trademarks or registered trademarks, and are used only for identification and explanation without intent to infringe.

Visit the Taylor & Francis Web site at  
<http://www.taylorandfrancis.com>

and the CRC Press Web site at  
<http://www.crcpress.com>

---

# Contents

Preface .....	xi
Author .....	xiii
Notation .....	xv
<b>Chapter 1</b> Introduction .....	1
1.1 Aggregation States of Matter .....	1
1.2 Nature of the Intermolecular Forces .....	2
1.3 Simple Potential Models .....	5
References .....	10
<b>Chapter 2</b> Some Basics on Statistical Mechanics .....	13
2.1 Virial Theorem and the Equation of State .....	13
2.2 Distribution Functions .....	15
2.3 Thermodynamic Properties in Terms of the Radial Distribution Function .....	22
2.4 Static Structure Factor .....	26
References .....	28
<b>Chapter 3</b> Overview of Computer Simulation Methods .....	31
3.1 Computer Simulations .....	31
3.2 Monte Carlo Method .....	32
3.2.1 Monte Carlo Method in the Canonical Ensemble .....	32
3.2.2 Monte Carlo Method in the Isothermal–Isobaric Ensemble .....	33
3.2.3 Monte Carlo Method in the Grand Canonical Ensemble .....	35
3.2.4 Configurational-Bias Monte Carlo .....	35
3.3 Molecular Dynamics Method .....	36
3.3.1 Algorithms for Solving the Equations of Motion .....	37
3.3.2 Molecular Dynamics Method in the Canonical Ensemble .....	40
3.3.3 Molecular Dynamics Method in the Isothermal–Isobaric Ensemble .....	42
3.3.4 Molecular Dynamics Method in the Grand Canonical Ensemble .....	44
3.4 Some Technical Details .....	46
3.4.1 Number of Particles .....	46
3.4.2 Periodic Boundary Conditions .....	46
3.4.3 Minimum Image Convention .....	46

3.4.4	Cutoff Distance of a Continuous Potential .....	46
3.4.5	Setting the Initial State .....	47
3.4.6	Equilibration .....	48
3.4.7	Setting the Length of the Steps .....	48
3.4.8	Saving Computational Time .....	49
3.4.9	Dealing with Long-Range Interactions .....	49
3.5	Thermodynamic and Structural Properties from Computer Simulation .....	50
3.6	Computer Simulation of Phase Equilibria .....	57
3.6.1	Temperature- and Density-Scaling Monte Carlo.....	57
3.6.2	NPT and NVT Plus Test Particle Insertion Methods.....	58
3.6.3	Gibbs Ensemble Simulation.....	59
3.6.4	Gibbs–Duhem Integration.....	59
3.6.5	Histogram-Reweighting Grand Canonical Monte Carlo Simulation.....	60
3.6.6	Pseudoensembles, Expanded Ensembles, and More .....	64
	References.....	66
<b>Chapter 4</b>	<b>Integral Equation Theories .....</b>	<b>73</b>
4.1	Ornstein–Zernike Equation .....	73
4.2	Closure Conditions .....	74
4.2.1	Simple Closures .....	75
4.2.2	Thermodynamically Self-Consistent Integral Equation Theories .....	77
4.2.3	Molecular Fluids .....	79
4.2.4	Algorithms for Numerical Solution of Integral Equation Theories .....	80
4.3	Universality of the Bridge Function .....	81
4.4	Integral Equation Perturbation Theories .....	84
4.4.1	Corrected Integral Equation Theories .....	84
4.4.2	Optimized Random Phase Approximation .....	84
4.4.3	Reference Integral Equation Theories .....	86
4.4.4	Perturbative Solutions of the Percus–Yevick and Mean Spherical Approximations .....	88
4.5	Some Results from Integral Equation Theories for Selected Potential Models .....	88
4.5.1	Square-Well Fluids .....	89
4.5.2	Hard-Core Yukawa Fluids .....	90
4.5.3	Soft-Sphere Fluids .....	91
4.5.4	Lennard–Jones Fluid .....	92
4.5.5	Nonspherical Potentials .....	96
	References.....	98

<b>Chapter 5</b>	Radial Distribution Function and Equation of State of the Hard-Sphere Fluid and Solid .....	107
5.1	Fluid and Solid Phases in the Hard-Sphere System .....	107
5.2	Scaled Particle Theory .....	108
5.3	Solution of the Percus–Yevick Equation .....	110
5.4	Rational Function Approximation .....	116
5.5	First-Order Mean Spherical Approximation .....	121
5.6	Equation of State and Radial Distribution Function of the Hard-Sphere Solid .....	123
	References .....	129
<b>Chapter 6</b>	Free Energy Perturbation Theories for Simple Fluids and Solids .....	133
6.1	Series Expansion of the Free Energy .....	133
6.2	Calculation of the Perturbation Terms by Computer Simulation .....	137
6.3	Perturbation Theories for Hard-Core Potentials .....	139
6.3.1	First-Order Perturbation Theory .....	139
6.3.2	van der Waals and Related Approximations .....	141
6.3.2.1	van der Waals Equation .....	141
6.3.2.2	Haar–Shenker–Kohler Approximation .....	142
6.3.2.3	Generalized van der Waals Theory .....	142
6.3.3	Barker–Henderson Second-Order Perturbation Theory .....	144
6.3.3.1	Barker–Henderson Macroscopic and Local Approximations .....	144
6.3.4	More Advanced Approximation for the Second-Order Term .....	144
6.3.5	Higher-Order Perturbation Theory .....	146
6.4	Perturbation Theories for Soft-Core Potentials .....	146
6.4.1	Barker–Henderson Perturbation Theory for Soft-Core Potentials .....	147
6.4.2	Weeks–Chandler–Andersen Perturbation Theory .....	148
6.4.3	Song–Mason Approximation .....	150
6.4.4	Variational Perturbation Theory .....	152
6.5	Mode Expansion .....	152
6.6	Hierarchical Reference Theory .....	156
6.7	Using Non-Hard-Sphere Reference System .....	158
6.8	Results for Some Potential Models .....	160
6.8.1	Square-Well Fluids .....	160
6.8.2	Hard-Core Yukawa Fluids .....	162

6.8.3	Crystalline Solids with the Sutherland Potential .....	163
6.8.4	Soft-Sphere Fluids .....	165
6.8.5	Lennard–Jones Fluid .....	168
	References .....	170
<b>Chapter 7</b>	<b>Perturbation Theories for Simple Fluid Mixtures .....</b>	<b>177</b>
7.1	Real and Ideal Mixtures .....	177
7.2	Conformal Mixtures .....	178
7.3	<i>n</i> -Fluid Models for Conformal Mixtures .....	181
7.3.1	Random Mixture Model .....	182
7.3.2	van der Waals One-Fluid Model .....	183
7.3.3	Hard-Sphere Expansion .....	184
7.3.4	van der Waals Two-Fluid Model .....	184
7.3.5	Three-Fluid Models .....	185
7.4	Extension to Mixtures of Perturbation Theories for Monocomponent Systems .....	186
7.4.1	Extension to Mixtures of Integral Equation and Integral Equation Perturbation Theories .....	186
7.4.2	Extension to Mixtures of Free Energy Perturbation Theories .....	187
7.5	Mixtures of Additive Hard Spheres .....	189
7.5.1	Scaled Particle Theory for Additive Hard-Sphere Fluid Mixtures .....	190
7.5.2	Percus–Yevick Theory for Additive Hard-Sphere Fluid Mixtures .....	192
7.5.3	Some Improved Approximations .....	194
7.6	Mixtures of Nonadditive Hard Spheres .....	196
7.6.1	Scaled-Particle Theory for Nonadditive Hard-Sphere Mixtures .....	198
7.6.2	Integral Equation Theories for Nonadditive Hard-Sphere Mixtures .....	200
7.6.3	Perturbation Theories for Nonadditive Hard-Sphere Mixtures .....	201
7.7	Other Simple Mixtures .....	206
	References .....	209
<b>Chapter 8</b>	<b>Perturbation Theories for Molecular Fluids .....</b>	<b>215</b>
8.1	Extension of the Free Energy Perturbation Theory to Fluids with Anisotropic Interactions .....	215
8.2	Scaled-Particle-Like Approaches for Hard-Body Molecular Fluids .....	216
8.2.1	Scaled Particle Theory for Hard Convex Body Fluids .....	216

8.3	Percus–Yevick Theory for Hard-Sphere Chain Fluids.....	222
8.4	Generalized Flory Theories for Hard-Sphere Chain Fluids .....	228
8.4.1	Flory and Flory–Huggins Lattice Models for Chain Molecular Fluids .....	228
8.4.2	Extension of the Flory and Flory–Huggins Theories to Continuous Space .....	230
8.4.3	Generalized Flory-Dimer Theory .....	231
8.5	Wertheim’s Perturbation Theory for Hard-Sphere Chain Fluids .....	234
8.5.1	Wertheim’s First-Order Perturbation Theory.....	234
8.5.2	Wertheim’s Second-Order Perturbation Theory.....	239
8.5.3	Resummed Thermodynamic Perturbation Theory .....	240
8.5.4	Correction to Account for Monodispersity .....	241
8.5.5	Dimer Correction .....	242
8.5.6	Sequential Polymerization .....	244
8.6	Extensions to Linear Fused Hard-Sphere Chains .....	249
8.7	Perturbation Theories for Molecular Fluids with Dispersive Forces.....	255
8.7.1	Perturbed Hard-Chain Theory.....	255
8.7.2	Perturbed Hard-Sphere-Chain Theory .....	257
8.7.3	Boublík–Alder–Chen–Kreglewski Equation of State .....	257
8.7.4	Chain-of-Rotators Equation of State .....	258
8.7.5	Statistical Associating Fluid Theory .....	259
8.7.5.1	SAFT-D .....	260
8.7.5.2	SAFT-VR.....	261
8.7.5.3	PC-SAFT.....	262
8.7.5.4	Soft-SAFT.....	262
8.7.5.5	GC-SAFT .....	263
8.8	Non-Isotropic Phases.....	265
	References.....	272
<b>Chapter 9</b>	<b>Inhomogeneous Systems .....</b>	<b>281</b>
9.1	Fundamentals of the Density Functional Formalism .....	281
9.2	Some Density Functional Approximations .....	283
9.2.1	Perturbation Expansions.....	283
9.2.2	Weighted Density Approximation and Related Theories .....	286
9.2.3	Reference Functional Approach .....	290
9.3	Fundamental Measure Theory .....	291
9.4	Simple Fluids and Solids.....	296
9.4.1	Local Density of the Solid.....	296



9.4.2	<i>n</i> -Particle Direct Correlation Functions of the Homogeneous Fluid .....	297
9.4.3	Freezing of Hard Spheres .....	299
9.4.4	Relative Stability of the sc, bcc, fcc, and hcp Phases of Hard Spheres.....	303
9.4.5	Hard-Sphere Glass .....	305
9.4.6	Hard-Sphere Mixtures .....	306
9.4.7	Systems with Soft and Attractive Potentials .....	308
9.4.7.1	Square-Well Potential .....	308
9.4.7.2	Hard-Core Yukawa Potential .....	310
9.4.7.3	Soft-Sphere Potential .....	311
9.4.7.4	Lennard–Jones Potential .....	312
9.5	Surfaces and Interfaces .....	314
9.5.1	Density Profiles near a Hard Wall .....	314
9.5.2	Surface Melting .....	322
9.5.3	Liquid–Vapor Interface.....	325
9.6	Inhomogeneous Systems with Anisotropic Interactions.....	327
	References.....	331

<b>Chapter 10</b>	Overview to Perturbation Theories for More Complex Systems .....	341
10.1	Fluids near the Critical Point .....	341
10.2	Liquid Metals, Molten Salts, and Electrolyte Solutions ....	347
10.2.1	Liquid Metals .....	347
10.2.2	Molten Salts and Electrolyte Solutions.....	352
10.3	Colloids and Colloid-Polymer Mixtures .....	353
10.3.1	Depletion Potentials .....	353
10.3.2	Effective One-Component Approach for a Hard-Sphere Colloidal Model .....	360
10.3.3	Effective One-Component Approach in Simple Colloid-Polymer Mixtures .....	362
10.3.4	Charge-Stabilized Colloidal Suspensions .....	364
10.4	Aqueous Protein Solutions .....	366
	References .....	372
<b>Index</b>	.....	379