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Statistical Mechanics

Part A: Equilibrium Techniques

Edited by
Bruce J. Berne

Statistical Mechanics

Part A: Equilibrium Techniques

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Preface

The last decade has been marked by a rapid growth in statistical mechanics, especially in connection with the physics and chemistry of the fluid state. Our understanding in these areas has been considerably advanced and enriched by the discovery of new techniques and the sharpening of old techniques, ranging all the way from computer simulation to mode–mode coupling theories.

Statistical mechanics brings together under one roof a broad spectrum of mathematical techniques. The aim of these volumes is to provide a didactic treatment of those techniques that are most useful for the study of problems of current interest to theoretical chemists. The emphasis throughout is on the techniques themselves and not on reviewing the enormous literature in statistical mechanics. Each author was charged with the following task. Given N pages, (a) pose the problem, (b) present those aspects of the particular technique that clearly illustrate its internal workings, (c) apply the technique to the solution of several illustrative examples, and (d) write the chapter so that it will enable the reader to approach key citations to the literature intelligently.

These volumes are designed for graduate students and research workers in statistical mechanics. Nevertheless, because of the range of techniques and their general utility, they should be useful in other areas as well.

The choice of topics was dictated not only by the taste and interests of the editor, but also by the proviso that there did not already exist a didactic treatment in the literature. The topics fall rather neatly into two categories: equilibrium and nonequilibrium properties of fluids. Thus, this volume is devoted to equilibrium techniques and the companion volume to the nonequilibrium techniques.

This volume begins with a chapter on modern cluster methods in equilibrium statistical mechanics and shows how topological reduction can be used to renormalize bonds. A general discussion of renormalization methods is given and the formalism is applied to the study of polar gases, ionic solutions, perturbation theory of fluids, hydrogen-bonded fluids, and integral equations.

This chapter is followed by two chapters on the treatment of fluids with long-range forces. In particular, special techniques are presented for treating

Coulomb forces and permanent multipolar forces. These chapters draw on some of the concepts developed in the first chapter.

Much of what is known about the fluid state springs from Monte Carlo studies of model fluids. Chapter 4 is concerned with the application of Monte Carlo techniques to the study of fluids with short-range forces. Chapter 5 extends this method to the study of fluids with long-range forces and introduces some innovative techniques. The volume closes with a chapter on nucleation theory.

Bruce J. Berne

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Statistical Mechanics

Part A: Equilibrium Techniques

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Contents of Volume 6

Chapter 1. Molecular Dynamics Techniques for Hard Core Systems

Jerome J. Erpenbeck and William W. Wood

Chapter 2. Molecular Dynamics Methods: Continuous Potentials

J. Kushick and B. J. Berne

Chapter 3. The Kinetic Theory of Gases

J. R. Dorfman and H. van Beijeren

Chapter 4. Renormalized Kinetic Theory of Dense Fluids

Gene F. Mazenko and Sidney Yip

Chapter 5. Projection Operator Techniques in the Theory of Fluctuations

Bruce J. Berne

Chapter 6. Principles of Mode–Mode Coupling Theory

T. Keyes

Chapter 7. Global Analysis of Nonlinear Chemical Kinetics

Leon Glass

Contents of Volume 5

Contents of Volume 6 xv

Chapter 1. Cluster Methods in Equilibrium Statistical Mechanics of Fluids
Hans C. Andersen

1. Introduction 1
2. Graph-Theoretic Definitions 2
   2.1. Definition of a Graph and the Ideas of Topological Equivalence and Connectivity 2
   2.2. Point Functions, Bond Functions, and the Definition of the Value of a Graph 6
3. Partition Function, Pair Correlation Function, and Their Graphical Representation 9
   3.1. Statistical-Mechanical Definitions 9
   3.2. Cluster Expansion Expressions for $\mathcal{A}$ and g 11
4. Topological Reduction 15
5. General Philosophy of the Renormalization Method 19
   5.1. Motives for the Use of Renormalization 19
   5.2. Strategies for Dealing with the Cluster Series for a Particular Fluid 20
6. Applications of Cluster Theory 21
   6.1. Low-Density Virial Series for Nonpolar Fluids 21
   6.2. Mayer Theory of Ionic Solutions 23
   6.3. Blip Function Theory 25
   6.4. Perturbation Theory of Fluids 29
   6.5. γ-Ordering and Γ-Ordering 31
   6.6. Optimized Cluster Theory 35
   6.7. Hydrogen-Bonded Fluids 38

7. Concluding Remarks 43
References 44

Chapter 2. Fluids with Long-Range Forces: Toward a Simple Analytic Theory
G. Stell

1. Introduction 47
2. Some General Features of the Fluids under Consideration . . . 49
3. Large λ–Small λ Interpolation; Padé Approximants 55
4. Large r–Small r Interpolation; The Mean Spherical Approximation 57
5. Beyond the MSA 57
   5.1. Γ Ordering, Nodal Contraction, Nodal Ordering, Nodal Approximation 57
   5.2. Mixed Perturbation Theory 70
6. Summary of Results 71
   Appendix 77
   References 82

Chapter 3. Electrolyte Solutions at Equilibrium
Harold L. Friedman and William D. T. Dale

1. Introduction 85
2. Models for Ionic Solutions 86
   2.1. Hamiltonian Models 86
   2.2. Choice of Level 86
   2.3. Principal Features of Interionic Forces 88
   2.4. Additional Contributions to Interionic Forces 89
   2.5. Current Research on Interionic Forces in Solution 91
3. Measurable Properties of Solutions at Equilibrium 91
   3.1. Solvation Coefficients 91
   3.2. Thermodynamic Excess Functions. Solutions of a Single Electrolyte 92
   3.3. Thermodynamic Excess Functions. Mixed Electrolytes . . 93
   3.4. Thermodynamic Excess Functions. Mixtures of Electrolytes with Nonionic Solutes 94
   3.5. Partial Structure Factors 95

此为试读,需要完整PDF请访问: www.ertongbook.com

4. McMillan–Mayer Theory 95
4.1. Basic Grand Ensemble Equations 95
4.2. McMillan–Mayer Theory 96
4.3. More General Results 99
4.4. General Significance of the MM Theory 99
5. Thermodynamic Aspects of the McMillan–Mayer Theory . . . 101
5.1. Solvation Thermodynamics 101
5.2. Thermodynamic Excess Functions. LR to MM Conversions 102
5.3. Thermodynamic Excess Functions in the MM System . . 104
6. Cluster Expansions 105
6.1. Graph Theory 105
6.2. Graphical Representation of the Grand Partition Function 107
6.3. Ursell Functions of the W_N 108
6.4. Cluster Functions 112
6.5. Rooted Ursell Functions 113
6.6. Cluster Expansion of A^{ex} 115
6.7. Discussion of the Cluster Expansion of A^{ex} 116
6.8. Mayer Resummation 118
7. Integral Equations 123
7.1. Ornstein–Zernike Equation 123
7.2. Integral Equations for Nonionic and Ionic Systems . . . 124
7.3. Mean Spherical Approximation 128
7.4. Other Approximation Methods 129
7.5. Quality Tests 129
References 132

Chapter 4. A Guide to Monte Carlo for Statistical Mechanics: 1. Highways

J. P. Valleau and S. G. Whittington

1. Introduction 137
2. The Monte Carlo Method 139
2.1. The Need for Refined Monte Carlo Sampling 139
2.2. Importance Sampling 140
2.3. The Metropolis Sampling Scheme 141
2.4. Choice of the Transition Matrix 144
3. Some Practical Details 146
3.1. Typical Procedures 146
3.2. Other Ensembles 148
3.3. Nonfluid Problems 149

4. Boundary Conditions 150
4.1. Avoiding Surfaces: Periodic Boundary Conditions . . . 150
4.2. Size and Shape of the Sample 151
4.3. Configurational Energy Estimation 153
5. Conclusion 161
Appendix A: Random Number Generators 161
Appendix B: Ewald Potential Technique 163
References 166

Chapter 5. A Guide to Monte Carlo for Statistical Mechanics: 2. Byways
J. P. Valleau and G. M. Torrie

1. Introduction 169
2. Estimations of Free Energy and Entropy 170
2.1. Salsburg and Others 171
2.2. Coldwell 171
2.3. Thermodynamic Integration 172
2.4. Communal Free-Energy Estimation 174
2.5. Widom's Particle Insertion Method 175
2.6. Grand Canonical Approach 175
2.7. McDonald and Singer: Energy Density Functions 177
2.8. Multistage Sampling 178
2.9. Umbrella Sampling Methods 178
3. Quantum Mechanical Calculations 182
3.1. Variational Calculations 182
3.2. Numerical Solution of Schrödinger's Equation 184
4. Microscopic Studies 185
4.1. Gas–Liquid Interface 185
4.2. Interionic Mean Forces 187
5. Conclusion 190
References 191

Chapter 6. Nucleation Theory
J. J. Burton

1. Introduction 195
2. Mathematical Formalism 198
2.1. The Nucleation Problem 199

2.2. McDonald's Trick 201
2.3. An Alternative Trick 204
2.4. Some Remarks 207
3. Homogeneous Gas Phase Nucleation 208
3.1. Capture Rates 209
3.2. Equilibrium Cluster Concentrations—Statistical-Mechanical Considerations 209
3.3. The Drop Model 210
3.4. Classical Nucleation Theory 211
3.5. Criticisms of the Drop Model and Classical Nucleation Theory 215
3.6. Statistical-Mechanical Emendations 216
3.7. Modification of the Surface Free Energy 217
3.8. A Microscopic Approach to the Cluster Free Energy . . . 219
3.9. A Proposed New Approach 221
4. Condensation of Water on Ions 224
5. Void Nucleation in Nuclear Reactor Materials 228
References 232

Author Index 235
Subject Index 239

1

Cluster Methods in Equilibrium Statistical Mechanics of Fluids

Hans C. Andersen

1. Introduction

Cluster expansion methods have proven to be exceedingly useful and general for discussing the equilibrium structure and thermodynamic properties of fluids. They have been used to rederive older results, such as the virial expansions for gases[1] and the Debye–Hückel theory for ionic solutions,[2] and then extend them in a systematic way. They have been used to derive approximate results that had not been obtained in other ways, such as the Γ and γ expansions[3] and the EXP approximation[4] for classical fluids. Moreover, they provide a unifying language for discussing and comparing the variety of theories of liquids that have been proposed; for example, many integral equations such as the Percus–Yevick equation[5] and the mean spherical model equation[6–8] for the pair correlation function of a fluid can be regarded as devices for summing certain diagrams in a cluster series.

In the early work of Mayer,[1,2] the theoretical manipulation of cluster expansions involved solving a number of rather complex combinatorial problems and was formidable enough to deter all but the most stalwart of theoreticians. A curious aspect of this work is that the route from a rather simple starting point (the formal definition of a canonical ensemble partition function) to an elegant and simple result (an expression for the free energy or pressure in terms of irreducible cluster integrals) required such a complicated path. It was as if all the complications introduced in the combinatorial analysis magically

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disappeared at the end to give a simple answer. The work of Morita and Hiroike[9] (see also Stell[10]) cleared up many of the difficulties by pointing out some of the formal properties of cluster series that are responsible for obtaining simple results. In the more recent work on cluster expansions, combinatorial problems play a very minor role; they are needed for defining cluster series and for evaluating cluster integrals but not for the formal manipulation of cluster series.

In this article we will deal with graphical methods for calculating the free energy and pair correlation function for homogeneous classical fluids consisting of atoms and rigid molecules away from the critical point. The formalism for fluids of molecules with orientation-dependent forces and for mixtures of molecules is no more complicated than for atomic liquids, and so we will include these features in the discussion. We will discuss some general properties of cluster expansions and then discuss techniques for reexpressing cluster series in forms that lead to computationally tractable and accurate approximations for fluids of various types.

Section 2 defines the graph-theoretic terms we will use. In Section 3, the statistical-mechanical quantities related to fluid structure and thermodynamics are defined and are expressed in terms of cluster expansions. Section 4 contains a discussion of "topological reduction," which is the basic theoretic tool for manipulating cluster expansions. Section 5 discusses the various strategies used in applying cluster theory to particular problems. In Section 6, some examples are discussed to illustrate the various strategies. Section 7 contains some suggestions for further reading.

Two other chapters in this volume, namely, Chapter 2 by Stell and Chapter 3 by Friedman and Dale also contain discussions of particular applications of cluster expansion theory.

2. *Graph-Theoretic Definitions*

In this section we will define some of the important terms associated with the graphs in cluster expansion theory.

2.1. Definition of a Graph and the Ideas of Topological Equivalence and Connectivity

A *graph* is a collection of *points* and *bonds* that connect these points. In a pictorial representation of a graph, a point is drawn as a small circle and a bond as a line from one circle to another. (In some applications, it is convenient to define bonds that connect three or more points but we will not discuss this possibility here.) There are two different kinds of points, namely, *root points*

and *field points*. Root points are represented as open circles and field points as filled circles. (In some applications there is more than one type of root and field point, but we will not consider this here.) In some applications, there is only one type of bond, which is usually represented as a solid line. In other applications, there is more than one type of bond, and so we might use a solid line to denote one type of bond, a dashed line to represent the second type, etc. (For present applications, bonds have no intrinsic direction.) For theoretical manipulations in cluster theory, it is usually most convenient to deal with graphs in which the root points are labeled but the field points are unlabeled. That is, each root point is given a label, usually a number, and no two roots have the same label. Unless otherwise specified, all graphs discussed in this article are of this type. Some examples of graphs are given in the various figures.

We now wish to consider the idea of whether two graphs are *topologically different* or *topologically equivalent*. We will first discuss this idea informally and then give a more precise definition.

First of all, the question of whether two graphs are topologically equivalent or different arises only when they have the same number of root points and those roots have the same set of labels. Roughly speaking, two graphs are topologically equivalent if one can be "distorted" in such a way that it is superimposable on the other. To envisage the types of "distortions" that are allowed, imagine the points as buttons and the bonds as flexible rubber bands that connect the buttons. The buttons may be freely moved around on the graph, and when they move they drag along the ends of any rubber bands that are attached to them. The rubber bands can freely pass through each other, however. Some examples of topologically equivalent graphs are given in Fig. 1.

To define this concept more precisely, we need to define a labeled graph. A *labeled graph* has exactly the same definition as that given above for a graph, except that the field points (if any) as well as the root points have labels, usually numbers, and no two points have the same label. It is easy to define topological equivalence for labeled graphs. *Two labeled graphs*, which have the same number of root points, the same set of labels on the root points, the same

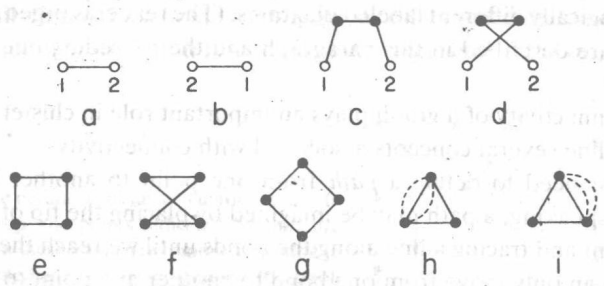

Fig. 1. Examples of topologically equivalent graphs. Graphs a and b are equivalent; as are c and d; e, f, and g; h and i. (The symmetry numbers of graphs a–i are 1, 1, 1, 1, 8, 8, 8, 2, and 2, respectively.)

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