STATISTICAL MECHANICS OF PHASES, INTERFACES, AND THIN FILMS

H. Ted Davis
CONTENTS

1 / Kinetic Theory of Dilute Gases in Equilibrium  1
1.1 Introduction  1
1.2 Equations of State for Pressure and Energy of an Ideal Monatomic Gas  3
1.3 Replacement of Time Averages by Ensemble Averages  6
1.4 Some Definitions from Probability Theory  8
1.5 Maxwell Velocity Distribution  12
1.6 Distribution and Mean Values Derived from Maxwell Distribution  17
1.7 Mean Free Path and Mean Collision Frequency for Rigid Sphere Molecules  23
1.8 Effusion  29
1.9 Evaporation and Chemical Reaction Rates  34
1.10 Experimental Tests of Maxwell's Distribution Law  40
1.11 The Boltzmann Factor and Barometric Formula  43
1.12 Waterson's Contribution to Kinetic Theory  47
    Supplementary Reading  49
    Exercises  49
    References  52

2 / The Elements of Ensemble Theory  55
2.1 Introduction  55
2.2 Intermolecular Forces  55
2.3 Quantum Mechanics of Simple Systems  59
    2.3.1 Particle in a Box  60
    2.3.2 Noninteracting Particles in a Box  62
    2.3.3 Rigid Rotator  62
    2.3.4 One-Dimensional Harmonic Oscillator  64
    2.3.5 A Model Diatomic Molecule in a Box  65
    2.3.6 $N$ Noninteracting Diatomic Molecules of the Type Considered in Case 5  69
    2.3.7 Energy of Hydrogen Atom in a Box  70
    2.3.8 $N$ Noninteracting Hydrogen Atoms in a Box  71
    2.3.9 A Polyatomic Model That Includes Electronic States  71
2.4 Postulates of Ensemble Theory  73
2.5 Canonical Ensemble  74
2.6 Grand Canonical Ensemble  83
2.7 Microcanonical Ensemble  87
9.1 Calculus of Variations and Functional Derivatives 425
  9.1.1 Functional Differentiation 425
  9.1.2 Functional Taylor’s Series 431
  9.1.3 Chain Rule and Inverse Functional Derivative 432
  9.1.4 Implicit Functional Theorem 433
  9.1.5 Functional Differential 433
  9.1.6 Conditions for Extremum for a Functional 434
  9.1.7 Functional Integration 434
9.2 Density Distributions and Correlation Functions 435
9.3 Homogeneous Fluids: Some Exact Results 442
9.4 Homogeneous Fluids: Approximate Theories 449
  9.4.1 Mean Spherical Approximation 449
  9.4.2 PY Approximation 454
  9.4.3 Hypernetted Chain Approximation 454
  9.4.4 Comparison of HNC, PY, and the BGYK Approximations 455
  9.4.5 Hard Sphere Mixtures 457
  9.4.6 Perturbation Approximations 462
9.5 Inhomogeneous Fluids: Some Exact Results 466
Supplementary Reading 469
Exercises 469
References 472

10 / Confined One-Dimensional Fluids 473
10.1 Thermodynamic Properties of Hard-Rod Fluids Between Rigid Walls 473
  10.1.1 Evaluation of Partition Functions and Thermodynamic Functions 473
  10.1.2 Pore Occupancy and Disjoining Pressure of a Pore Fluid 476
10.2 Density Distribution Functions for Hard-Rod Fluids in Arbitrary External Fields 482
10.3 Computation of Density Distributions of Inhomogeneous Hard-Rod Fluids 493
  10.3.1 Reformulation of Integral Equations for Density Distributions 493
  10.3.2 Numerical Methods 496
  10.3.3 Applications 499
10.4 Confined Tonks–Takahashi Fluids 507
  10.4.1 Fluids Confined and in the Presence of an Arbitrary External Field 507
  10.4.2 One-Component Fluids: No External Field (v(x) = 0) 511
Supplementary Reading 518
11 / Density Functional Theory of Fluid Interfaces 521
11.1 Local Density Functional Free Energy Model 521
  11.1.1 The van der Waals Model 521
  11.1.2 A Modified VDW Model 523
  11.1.3 An Approximate Density Functional (ADF) Model 525
  11.1.4 Density Gradient Theory 526
11.2 Local Density Functional Theory of Planar Fluid–Fluid Interfaces 528
11.3 Liquid–Vapor Interfaces: One-Component Fluids 532
11.4 Liquid–Vapor Interfaces: Multicomponent Fluids 536
11.5 Liquid–Liquid Interfaces 550
  Supplementary Reading 553
Exercises 554
References 555

12 / Density Functional Theory of Confined Fluids 557
12.1 Nonlocal Density Functional Free Energy Models 557
  12.1.1 The Generalized VDW Model 561
  12.1.2 The Generalized Hard-Rod Model 562
  12.1.3 The Tarazona Model 562
  12.1.4 The Curtin–Ashcroft Model 564
  12.1.5 The Meister–Kroll Model 565
  12.1.6 Multicomponent Generalizations of the Models 567
12.2 Simple Fluids Confined to Slit Pores 570
12.3 Interactions Between Electrically Charged Confining Surfaces 578
  12.3.1 The Contact Theorem 578
  12.3.2 Disjoining Pressure of Electrical Double Layer: DLVO Theory 580
  12.3.3 Disjoining Pressure of Electrical Double Layer: Density Functional Theory 589
  Supplementary Reading 595
Exercises 595
References 597

13 / Thin Films and Wetting Transitions 599
13.1 Introduction 599
13.2 Gradient Theory of Wetting Transitions 602
13.3 Nonlocal Density Functional Theory of Wetting Transitions 609
13.4 Local Density Functional Theory of Wetting Transitions 614
13.5 Experimental Studies of Wetting Transitions 621
  Supplementary Reading 625
Exercises 625
References 626

CONTENT / xv