

# Statistical Mechanics of Liquids

---

**Hidde Vuijk<sup>a</sup> Abhinav Sharma<sup>a,b</sup>**

<sup>a</sup>*Leibniz-Institut für Polymerforschung, Dresden, Germany*

<sup>b</sup>*TU Dresden*

*E-mail:* [vuijk@ipfdd.de](mailto:vuijk@ipfdd.de), [sharma@ipfdd.de](mailto:sharma@ipfdd.de)

---

## Contents

<b>1</b>	<b>Introduction</b>	<b>2</b>
1.1	Course Outline	2
<b>I</b>	<b>Basics</b>	<b>3</b>
<b>2</b>	<b>Basic Statistical Mechanics</b>	<b>4</b>
2.1	Ensembles	4
2.1.1	The Microcanonical Ensemble	4
2.2	Perfect Gases	4
<b>II</b>	<b>Core Concepts in Liquids State Theory</b>	<b>5</b>
<b>3</b>	<b>Imperfect Gases</b>	<b>5</b>
<b>4</b>	<b>Distribution Functions</b>	<b>6</b>
4.1	From the Probability density to Correlation Functions	6
4.1.1	The Pair-Distribution Function from Scattering Experiments	6
4.2	The Potential of Mean Force	6
4.2.1	The Super-Position Approximation	6
4.3	The Ornstein-Zernike Equation	6
4.4	Density Expansions of Distribution Functions	6
<b>5</b>	<b>Integral Equations for <math>g(r)</math></b>	<b>7</b>
5.1	The Kirkwood Equation	7
5.2	The Born-Green-Yvon Equation	8
5.3	The Percus-Yevick Equation	8
5.4	Density Expansion of the Percus-Yevick Equation	8
5.5	The Hypernetted-Chain Equation	8
<b>6</b>	<b>Numerical Solutions</b>	<b>8</b>
6.1	The Percus-Yevick Equation	8
6.1.1	Coordinate Transformation	8
6.1.2	Iterative Scheme	8
6.2	BGY	8
6.2.1	Coordinate Transformation	8
6.2.2	Iterative Scheme	8

<b>7</b>	<b>Perturbation Theory</b>	<b>8</b>
7.1	General Theory and the Van Der Waals Equation	8
7.2	Barker-Henderson Theory	8
7.3	Chandler-Weeks-Anderson Theory	8
<b>III</b>	<b>Transport Processes</b>	<b>8</b>
<b>8</b>	<b>Continuum Mechanics</b>	<b>8</b>
8.1	Phenomenological Theory	8
8.2	Statistical Foundations	8
<b>9</b>	<b>Kinetic Theory</b>	<b>8</b>
<b>IV</b>	<b>Appendix</b>	<b>8</b>
<b>A</b>	<b>Python Implementation</b>	<b>8</b>

---

# **1 Introduction**

## **1.1 Course Outline**

Part I

# Basics

## **2 Basic Statistical Mechanics**

some intro

### **2.1 Ensembles**

#### **2.1.1 The Micrcanonical Ensemble**

### **2.2 Perfect Gasses**

## Part II

# Core Concepts in Liquids State Theory

## 3 Imperfect Gasses

## **4 Distribution Functions**

### **4.1 From the Probability density to Correlation Functions**

#### **4.1.1 The Pair-Distribution Function from Scattering Experiments**

### **4.2 The Potential of Mean Force**

#### **4.2.1 The Super-Position Approximation**

### **4.3 The Ornstein-Zernike Equation**

### **4.4 Density Expansions of Distribution Functions**



## 5 Integral Equations for $g(r)$

TO DO: OUTLINE  $\text{RHO}(\mathbf{r}_1, \mathbf{r}_2; \xi=0) = \dots$

### 5.1 The Kirkwood Equation

The goal of this section is to derive an integral equation for the pair-distribution function called the Kirkwood equation. For this, one can use a system with two kinds of particles, just as the system that was used to express the chemical potential using the pair-distribution function. ADD EQ. REF In this system the interaction potential of particle 1 with any of the other particles is scaled by  $\xi$ :

$$U_N(\mathbf{r}_1, \dots, \mathbf{r}_N) = \sum_{j=2}^N \xi u(\mathbf{r}_1, \mathbf{r}_j) + \sum_{\substack{i=2 \\ j>i}}^N u(\mathbf{r}_i, \mathbf{r}_j), \quad (5.1)$$

with  $0 \leq \xi \leq 1$ , so when  $\xi = 1$  it is a system of  $N$  identical interacting particles, and when  $\xi = 0$  it is a system consisting of one ideal particle and  $N - 1$  interacting particles. Because there are two species of particles in this system (particle 1 and the "normal" particles), this means that one can define two kinds of radial distribution functions: one for the distribution of the normal particles around particle 1, one for the distribution of the normal particles around another normal particle. In these notes, the difference between these two functions is indicated by the arguments. When  $\mathbf{r}_1$  is one of the arguments (or  $|\mathbf{r}_1 - \mathbf{r}_j|$  with  $j > 2$ ), it is the first kind; otherwise it is the second kind. When which distribution function is which is not clear from the arguments, I indicate the distribution function of the normal particles around particle 1 with  $g_{(1,n)}^{(n)}(\dots)$  and the other kind with  $g_{(n,n)}^{(n)}(\dots)$ .

The starting point is the identity

$$kT \ln \left( \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n; \xi) \right) = kT \ln \left( \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n; \xi = 0) \right) + \int_0^\xi d\xi' \frac{\partial}{\partial \xi'} kT \ln \left( \rho^{(n)}(\mathbf{r}_1, \dots, \mathbf{r}_n; \xi') \right). \quad (5.2)$$

All that is to be done is to work out what the derivative on the right hand side is.

- 5.2 The Born-Green-Yvon Equation
- 5.3 The Percus-Yevick Equation
- 5.4 Density Expansion of the Percus-Yevick Equation
- 5.5 The Hypernetted-Chain Equation
- 6 Numerical Solutions
  - 6.1 The Percus-Yevick Equation
    - 6.1.1 Coordinate Transformation
    - 6.1.2 Iterative Scheme
  - 6.2 BGY
    - 6.2.1 Coordinate Transformation
    - 6.2.2 Iterative Scheme
- 7 Perturbation Theory
  - 7.1 General Theory and the Van Der Waals Equation
  - 7.2 Barker-Henderson Theory
  - 7.3 Chandler-Weeks-Anderson Theory

## Part III

# Transport Processes

- 8 Continuum Mechanics
  - 8.1 Phenomenological Theory
  - 8.2 Statistical Foundations
- 9 Kinetic Theory

## Part IV

# Appendix

- A Python Implementation