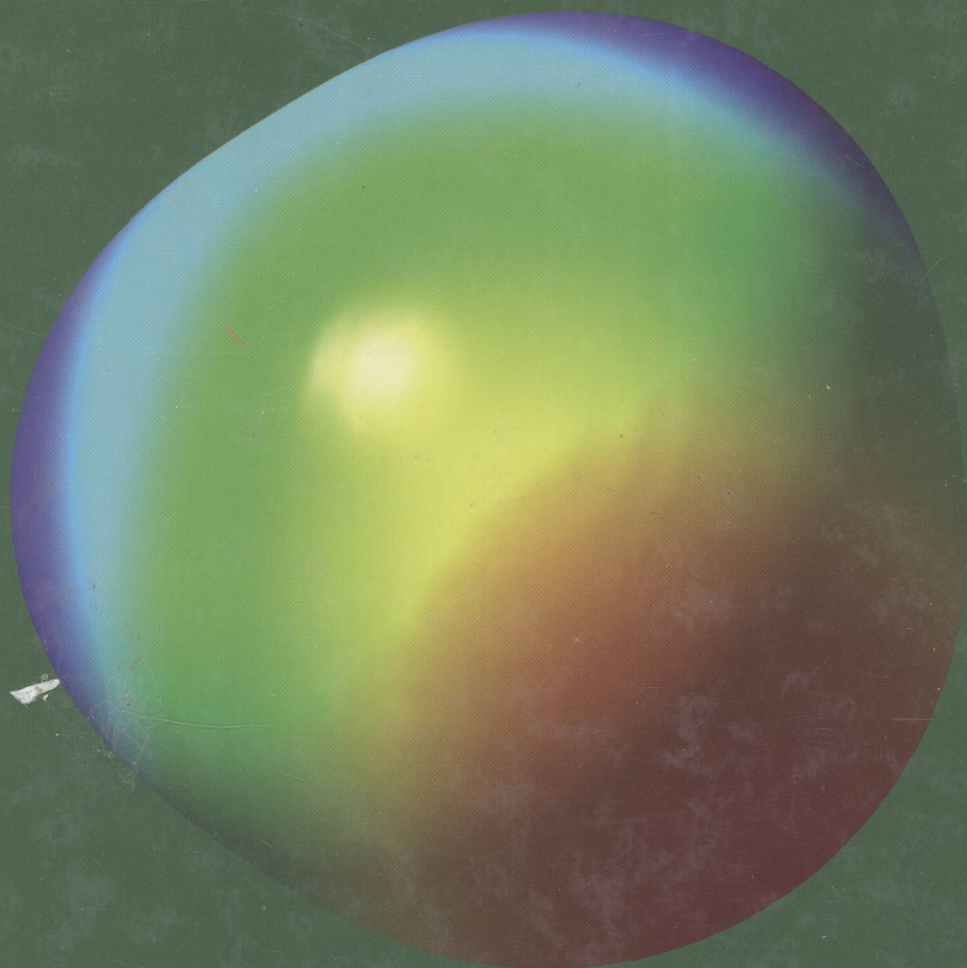


Molecular Models for Fluids

Klaus Lucas



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MOLECULAR MODELS FOR FLUIDS

KLAUS LUCAS

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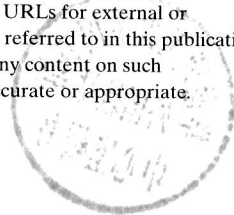
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MOLECULAR MODELS FOR FLUIDS

This book presents the development of modern molecular models for fluids from the interdisciplinary fundamentals of classical and statistical mechanics, of electrodynamics, and of quantum mechanics. The concepts and working equations of the various fields are briefly derived and illustrated in the context of understanding the properties of molecular systems. Special emphasis is devoted to the quantum mechanical basis, because this is used throughout in the calculation of the molecular energy of a system. The fundamentals are then used to derive models for various types of applications, ranging from ideal gas properties to excess functions and, finally, equations of state. The book is application-oriented and stresses those elements that are essential for practical model development. It is suited for graduate courses in chemical and mechanical engineering, physics, and chemistry, but may also, by proper selection, be found useful on the undergraduate level.

Professor Lucas has been the Chair of Thermodynamics at RWTH Aachen University since 2000. He previously held positions at the University of Stuttgart, at the University of Duisburg, and as the Scientific Director for the Institute of Energy and Environmental Technology, Duisburg Rheinhausen. He is a member of the Berlin Brandenburg Academy of Sciences and Humanities and acatech, German National Academy of Engineering, and is a consultant to various industrial companies in the fields of energy and chemical engineering. His research interests include the molecular modeling of fluids, energy systems analysis, and phase and reaction equilibria in fluids. He is the author or coauthor of more than 150 technical articles in scientific journals and is the author of a popular thermodynamics textbook.

To Gabi, Hanno, and Elena

Nomenclature

a) Roman Letters

A	free energy, Helmholtz potential, surface area
a_i	activity of component i
b	molecular size parameter
B	grand canonical potential, second virial coefficient
C	third virial coefficient
c	speed of light
C_p	isobaric heat capacity
C_v	isochoric heat capacity
d	hard sphere diameter
e	elementary charge
E	energy, electrical field strength
F	force
f	fugacity, Mayer function
G	Gibbs free energy and nonrandomness factor
g	degeneracy
$g(r)$	pair correlation function
H	enthalpy, Hamilton function
\hat{H}	Hamilton operator, Hamiltonian
H_i	Henry coefficient of component i
h	Planck's constant
I	moment of inertia, ionization potential
K	chemical equilibrium constant
k	Boltzmann constant
l	rotational quantum number
M	molar mass
m	mass
N	number of moles, molecules, surface contacts

N_A	Avogadro number
n	number density, number of segments or groups, translational quantum number
P	probability
p	pressure, momentum
Q	canonical partition function, charge
Q^C	configurational partition function
q	molecular partition function, nondimensional external surface, charge
R	gas constant
r	distance, volume segment of a molecule
S	entropy
T	thermodynamic temperature
U	internal energy, potential energy
V	volume
\hat{V}	interaction operator
v	molar volume, vibrational quantum number
x	mole fraction, coordinate
y	mole fraction, coordinate, packing density
Z	compressibility factor, charge number, state quantity
z	coordinate, coordination number

b) Greek Letters

α	dipole polarizability, nonsphericity parameter
β	$1/kT$
γ_i	activity coefficient of component i
ε	energy potential parameter, permittivity
η	packing density
θ	quadrupole moment, characteristic temperature, angle, surface fraction
λ	wave length, eigenvalue, perturbation parameter
μ	chemical potential, dipole moment, Joule–Thomson coefficient
ν	stoichiometric coefficient, frequency
Ξ	grand canonical partition function
Π	polarizability tensor
ϱ	charge density distribution, density
σ	distance potential parameter, surface charge density
Φ	Slater determinant
ϕ	pair potential energy, angle, orbital, fugacity coefficient, volume fraction
ψ	wavefunction, electrostatic potential
Ω	octopole moment, molecular arrangement
ω	orientational angle, acentric factor, exchange energy

c) Indices, Superscripts, Subscripts

a,b	interaction sites, charges
att	attractive
C	configurational
c	critical point
corr	corrections
d	hard sphere
E	excess
el	electronic
G	gas
h	hard body
i, j	component i, j in the mixture, quantum states
ig	ideal gas
ids	ideal dilute solution
ir	internal rotation
is	ideal solution
L	liquid
M	mixing
ntr	nontranslatory
P	perturbation contribution
r	rotation, reduced
ref	reference state
rep	repulsive
res	residual
s	saturated
t	triple point
tr	translatory
v	vibrational
0	reference
0i	pure component
"	saturated vapor
'	saturated liquid
*	conjugate complex, dimensionless
^	operator
α, β, κ	segments, groups, components

Preface

Many important industrial applications, as well as insight into the phenomena of nature, rely crucially on knowledge about fluid phase behavior. In space and other high-temperature industries, as well as in combustion processes, the properties of gases manifesting various types of reaction, including dissociation and ionization, are required. In chemical and environmental science and technology, phase and reaction equilibria of multicomponent mixtures form the basis of understanding the phenomena and designing synthesis, separation, and purification processes. Biotechnological downstream processing relies on the distribution properties of biomolecules in different phases of aqueous and organic solutions. Even in standard mechanical engineering equipment technology, such as refrigerator design, lack of data for new environmentally friendly refrigerants has proved to be a severe obstacle to technological progress. In all these cases, and many others, fluid phase properties form the basis of modern technological processes and detailed and quantitative knowledge of their properties is the premise of innovation. Experimental studies alone, although indispensable in the field of fluid system science, cannot serve these needs. The project of studying the fluid phase behavior of a multicomponent system experimentally is hopeless in view of the large number of data that would be needed. Instead, molecular models, which can be evaluated on a computer and make use of the limited data available to predict the fluid phase behavior in the full range of interest, are needed. Due to the broad availability of high-speed computers, such models can be quite ambitious, including use of quantum-chemical and molecular simulation computer codes.

Designing molecular models for fluid systems is an interdisciplinary field having its roots in classical mechanics, quantum chemistry, statistical physics, and electrodynamics. All models derived in this book originate from this basis. Their application to the computation of fluid phase behavior is executed with the help of the network of classical thermodynamic equations.

Chapter 1 is designed as an introduction to the subject. Some examples of macroscopic fluid behavior to be addressed in later chapters are discussed.

The variety of important phenomena and also the inadequacy of a purely macroscopic-experimental approach are clearly evident. Also, a first qualitative look is taken at molecular models and their relation to macroscopic properties.

Chapter 2 is devoted to the foundations of the field. The first section reviews the network of classical thermodynamic equations needed to compute the various aspects of fluid phase behavior. It is followed by a brief exposition of statistical mechanics, which provides the formal link between the macroscopic properties and a molecular model. The following section introduces the concepts of classical mechanics and applies them to established models of single molecule energy modes. The mechanical view of a molecular system is extended in the fourth section on classical electrostatics to include electrostatic interactions between molecular charges as a basis for the modeling of intermolecular forces. A section on quantum mechanics provides the necessary corrections and extensions to the classical mechanical and electrostatic results that make them applicable to molecular systems. In particular, it summarizes the quantum-chemical procedures now available for obtaining information about the geometrical structures of molecules as well as about charge distributions and associated molecular properties. A final section completes the foundations by developing the numerical path from the microscopic to the macroscopic world via computer simulation.

Chapter 3 considers as a first class of important applications the properties of the ideal gas. Besides deriving the ideal gas equation of state and general equations for the thermodynamic functions, it gives examples of predicted properties such as heat capacities and equilibrium constants on the basis of molecular properties derived from spectra or quantum-chemical computer codes.

Chapter 4 is concerned with models for the excess functions of liquid mixtures. The molecules of a liquid are assumed to interact via contacts over their surfaces. A statistical mechanical model is derived under well-defined approximations that can be used to predict the fluid phase behavior of liquid mixtures from information of the contact energies and its relation to some frequently used semiempirical models is discussed. The contact energies are either obtained from fitting the model to a large data base or, more recently, from quantum-chemical calculations.

More general applications over a large density range are considered in Chapter 5 on the basis of equation of state models. The intermolecular interactions must now be formulated as distance- and orientation-dependent functions. For low to moderate densities, the equation of state can be generally formulated in terms of a density expansion, with the expansion coefficients being expressed as integrals over the intermolecular potential functions. In the full density range, conformal potential models are derived, which can be corrected for specific intermolecular interactions by a perturbation approach. Rather sophisticated models with good predictive capacity can be formulated.

The text is designed for teaching first-year graduate courses within the curricula of mechanical and chemical engineering, physics, and chemistry. It aims at introducing the reader to the interdisciplinary scientific basis of the field, while at the same time making him or her acquainted with those approaches that have proven to be generally successful and are expected to be of lasting value. No effort is made to review the enormous plenitude of semiempirical models that have been published. Instead a unifying perspective is taken in deriving exemplary models systematically on the basis of the universally valid foundations. Actual calculations of molecular and macroscopic properties are today frequently done with the help of sophisticated computer codes. Although it does not discuss all details of the refined models included in such codes, the material in this book is meant to provide a basic understanding of them and lay the scientific basis on which future progress can be made.

During the preparation of the manuscript, of which some parts are based on my earlier book *Applied Statistical Thermodynamics* (Springer-Verlag, 1991), I have benefited from the contributions and the advice of some of my co-workers and colleagues. I wish to particularly acknowledge extensive discussions with K. Leonhard during the whole period of preparation of the book, as well as advice on important details by R. Bronneberg, R. Heggen, V. N. Nguyen, M. Singh, and J. Veverka. My colleagues D. Andrae, J. Groß, A. Klamt, G. Sadowski, and J. Vrabec critically read some parts of the manuscript and made helpful suggestions. The figures were prepared by T. Ameis and final production was executed by E. Frach and M. Lipková. I am very grateful to all of them.

Klaus Lucas
Aachen, Spring 2006

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1 Introduction

Our society relies on the use of energy and matter in a plenitude of different forms. They are produced from natural resources by technical processes of energy and matter conversion that have to be designed in an economically and ecologically optimum way. In these processes it is the fluid state of matter that dominates the relevant phenomena. In particular, the properties of fluid systems in equilibrium enter into the fundamental process equations and control the feasibility of the various process steps. Models for fluids in equilibrium are thus a prerequisite for any scientific process analysis. Although fluid models can be constructed entirely within the framework of a macroscopic theory on the basis of experimental data, it is clear that this approach is limited to those few systems for which enough data can be obtained. Typical examples are the working fluids of the standard power generation and refrigeration processes. The vast majority of technically relevant processes are, however, concerned with complex fluid systems that cannot be analyzed experimentally in sufficient detail with a reasonable effort. In such cases one must turn to the microscopic basis of matter and design a theory based on the molecular properties of a fluid that requires only few data or is even fully predictive. In this introductory chapter we present an overview of the challenges of this approach by presenting a review of macroscopic fluid phase behavior in equilibrium, along with the problems associated with obtaining the necessary information from data. We also give a first introduction to the primary concepts of the microscopic world, including a brief glance at the properties of real molecules and the philosophy behind formulating molecular models.

1.1 The Macroscopic World

Energy and matter conversion processes are part of the macroscopic world. They are carried out without taking notice of the underlying microscopic phenomena, much like breathing air and handling materials in every day life. Within the limits of the macroscopic world the properties of the associated fluid

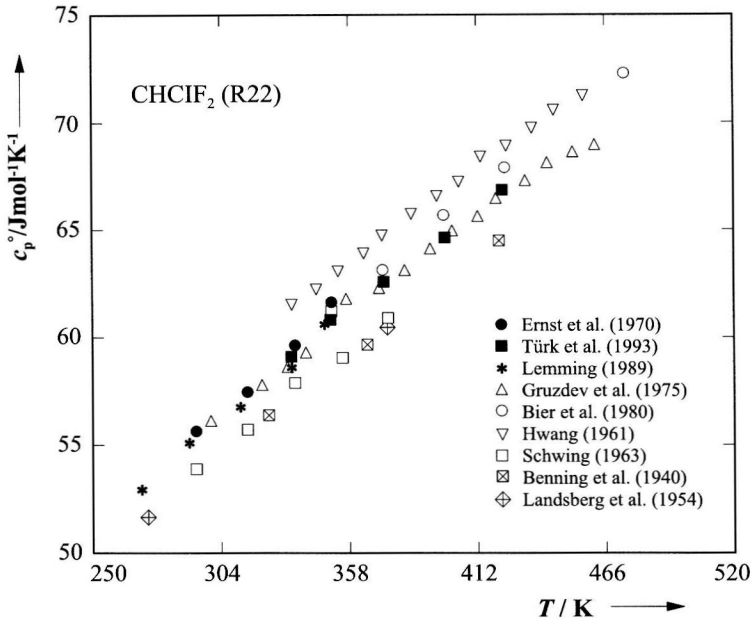


Fig. 1.1. Experimental data for the heat capacity of R22 (references to data given in [1]).

systems must be obtained from experiment. Fluid phase behavior is very plentiful, when studied over a wide range of temperature, pressure, and composition, and there are many fluids of technical interest. A few examples may illustrate this wealth of phenomena and the limitations of the macroscopic approach in providing the property information necessary to design technical processes.

An important property related to the energy conversion of a process is the heat capacity c_p . Fig. 1.1 shows the temperature dependence of the zero-pressure gaseous heat capacity of refrigerant R22 [1]. For calculations of refrigeration processes this property should be known to an accuracy of about 1%. The available experimental data reveal a spectrum of values differing by up to 10%. Little can be said about the reliability of the individual data sources on a purely macroscopic basis because experiments as a rule are not described in enough detail to assess their potential inaccuracies. Frequently, more recent data are given more credit than older data, and data from well-known laboratories are preferred over those from no-name sources, but this may be misleading, as was also found for R22. So, within the macroscopic approach to fluid properties and without an independent theoretical basis for evaluation of accuracy, we have to rely on the measured data as they are. We shall see, however, in Chapter 3 that molecular theory allows an unambiguous decision as to which set of data is correct and even a prediction when no data are available.

Proceeding to the large area of combustion processes, we need the heat capacities at much higher temperatures, but in particular we need properties related