studies in physical and theoretical chemistry 2

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PREFACE

In recent years, interest in exact statistical thermodynamic methods for the description of the equilibrium behaviour of real gases and liquids has increased considerably. Although no generally valid solutions to the problems have been found so far, significant progress has been made in characterizing systems that consist of simple types of molecules. Modern methods for the description of the behaviour of fluids are scattered in many articles in journals and in monographs; this might be a reason for the fact why the progress attained has not found its way adequately into the minds of workers in closely related areas of research.

In this monograph we have attempted to outline an overall view of the problems that may be encountered in the description of the state and the thermodynamic behaviour of fluids when employing the radial distribution function.

The book is the result of studies and lectures held at the Institute of Chemical Process Fundamentals of the Czechoslovak Academy of Sciences in Prague over a number of years; it is intended for advanced university students and research workers.

The contents have been divided into four chapters. The first chapter surveys statistical thermodynamic relationships for the description of the behaviour of fluids; the second outlines methods for the characterization of one-component systems, which are based on integral and integro-differential equations for the distribution functions. Perturbation methods for one- and multi-component systems are reviewed in Chapters 3 and 4, respectively. The less common mathematical devices and the purely mathematical parts of some treatments are given in the Appendices.

The Authors

LIST OF SYMBOLS

A	fluctuation term
B	2nd virial coefficient
C	3rd virial coefficient
	re-normalized potential
$D^{(N)}$	probability that an open system possesses exactly N molecules
E	internal energy
ΔE^{E}	excess internal energy
F	Laplace transform of the function $x\,c(x)$
	Helmholtz function (free energy)
F_0	Helmholtz function in the reference system
F^{id}	Helmholtz function in an ideal gas
G	Laplace transform of the function $x\,g(x)$
ΔG^{E}	excess Gibbs function
H	Heaviside step function
ΔH^{E}	excess enthalpy
HTA	high-temperature approximation
J	Bessel function
ᴊ	index denoting a component in a mixture
K	characteristic parameter in the pair potential of a power-law type
ᴋ	index denoting a component in a mixture
ʟ	index denoting a component in a mixture
LJ	Lennard-Jones pair potential
M_i	ith-order cumulant
MC	symbol for the data obtained by the Monte-Carlo method
N	number of molecules
	number of pairs separated by a certain distance
N'	number of molecules in a spherical shell around a central particle
$O(k)$	residue of a series which includes kth- and higher order terms
P	pressure in the system
P_0	pressure in the reference system
$P_N^{(N)}$	probability density of a configuration of N particles in a closed system
Q_N	configuration integral in a system with N particles
Q_i	ith-order perturbation term
S	entropy

ΔS^{E}	excess entropy
T	absolute temperature
T^*	molecularly reduced temperature
U	inverse Laplace transform of the function $x\,u(x)$
U_N	potential energy in a system with N particles
U_0	reference system potential energy
U_{p}	perturbation potential energy
V	volume
ΔV^{E}	excess volume
W_N	potential energy of a system in an external field
Y	$\exp[\beta u]\,g$
Z_N	canonical partition function
a	activity
b	excluded volume in the van der Waals equation
b_0	2nd virial coefficient of hard spheres
c	direct correlation function
c	“compressibility” form of the equation of state of hard spheres
c	ratio of the representative hard sphere diameter and the characteristic parameter σ
$\hat{c}$	Fourier transform of the function $c(x)$
d	representative hard sphere diameter
e	$\exp[-\beta u]$
f	Mayer function, $f = \exp[-\beta u] - 1$
f_{p}	Mayer function of the perturbation potential
g	radial distribution function
g_0	radial distribution function in the reference system
g_d	radial distribution function of hard spheres with diameter d
$g^{(n)}$	nth-order correlation function
$\boldsymbol{h}$	Planck's constant
h	total correlation function
$\hat{h}$	Fourier transform of the function $h(x)$
$_{\mathrm{hs}}$	index denoting hard sphere functions
$\boldsymbol{k}$	Boltzmann's constant
$\mathbf{k}$	wave vector
l. c.	local compressibility approximation
m	mass of a molecule
$_{m}$	exponent in power-law pair potentials
m. c.	macroscopic compressibility approximation
$_{\mathrm{p}}$	index denoting perturbational quantities
q	Fourier component of the density
$\boldsymbol{r}$	radius vector
r	absolute value of a distance

s. a.	superposition approximation
u	pair potential
$\hat{u}$	Fourier transform of the perturbation pair potential
v	modified pair potential
	screened pair potential
v	symbol for the virial form of the equation of state of hard spheres
$w^{(2)}$	potential of the average force
x	reduced distance
x_i	molar fraction of component i
y	$\pi \varrho d^3/6$
z	activity
	positional coordinate
$\mathfrak{A}, \mathfrak{B}, \mathfrak{M}, \ldots$	sets of graphs
$\Gamma, \Lambda, \ldots$	graphs
$\mathbf{H}, \mathbf{G}, \ldots$	matrices
$\langle\,\rangle$	mean value
$\langle\,\rangle_0$	value averaged over configurations of the reference system
Γ	gamma function
Ξ	grand canonical partition function
$\Xi_i[\mu]$	grand canonical partition function of a shell with radius R_i
α	parameter in the modified Barker-Henderson potential
β	$(kT)^{-1}$
γ	Euler's constant
	parameter in the pair potential
δ	Dirac function
	variation
ε	characteristic parameter in the pair potential
ζ	ratio of third powers of the representative hard sphere diameter and the characteristic parameter σ
η_{K}	modified number density of component K
λ	parameter in the pair potential
	thermal wavelength
μ	chemical potential related to one molecule
ξ	coupling parameter
ϱ	number density of particles
$\varrho^{(h)}$	hth-order generic distribution function
σ	characteristic parameter in the pair potential
φ	potential of the interaction with external field
χ	structure factor

INTRODUCTION

The description and prediction of equilibrium behaviour of fluids and fluid mixtures belong nowadays to the most challenging and perhaps also most significant goals at the boundary between physical chemistry and physics. This is especially due to the fact that a large proportion of chemical processes proceed in the liquid phase. From the theoretical point of view, an exact description of fluids (*i.e.*, real gases and liquids) represents the next important stage of development following the statistical thermodynamic interpretation of the behaviour of ideal gases and the perfect crystals. From a practical point of view, a knowledge of the statistical thermodynamic description of fluids, with the corresponding prediction of their thermodynamic behaviour, appears to be essential for contemporary methods for the design and control of processes in chemical technology.

A solution to the problem of the exact description of the behaviour of fluids involves two aspects: the interpretation of the intermolecular interactions and the determination of relationships between given intermolecular forces and the structure, *i.e.*, the spatial arrangement of particles in the fluid. Whereas the approximations for intermolecular interactions are obtained by quantum-mechanical methods, the solution to the second problem requires statistical thermodynamics.

Most of the theories of fluids can be divided roughly into two basic groups. The first group includes lattice theories, which start from an initially assumed structure of the system and neglect entirely the effects of molecular properties on this structure. A priori assumptions about the arrangement of the molecules then make it possible to introduce simplifying approximations into the calculation of the partition function that are analogous to those employed in the description of the perfect crystal. The lattice theories of liquids (a survey of which can be found elsewhere[8]) became, in the 1930s to 1950s the most frequently employed and successful method for the interpretation of fluid behaviour. They are now little used, except in the special case of their application to high-molecular-weight systems.

The second group includes theories that derive in a consistent manner the relationships that exist between the intermolecular forces and the structure of the system described in terms of distribution functions. However, the problem of finding these relationships is complicated, both conceptually and mathematically, so that it can be solved only in stages which subsequently encompass an increasingly wider range of systems (monatomic fluids, polar substances, molecular fluids, etc.) and enable the description in an ever wider range of thermodynamic variables.

The first stage in this development is the statistical thermodynamic description of the behaviour of simple fluids, *i.e.*, of systems composed of monatomic or small, approximately spherical, polyatomic molecules whose intermolecular forces are of the central type (*i.e.*, they depend only on the distance between the centres of the individual molecules).

The characterization of equilibrium behaviour is relatively simple for these systems; it has been subjected to intensive study and constitutes the basis for formulations of theories of polar substances[35] and systems with complex molecules. The significance of such studies is also emphasized by the fact that, empirically, the character of the equilibrium behaviour of the simplest liquid and real gas systems, *e.g.* rare gases, is not too different from that of more complex ones.

Since theories of simple fluids are still under development we cannot present here a complete and fully logically built survey. In this monograph we have, therefore, tried rather to outline the contemporary state of development, to pick out the main concepts and to show the connections among them and the possibilities of the individual treatments proposed for the simplest systems. Methods for treating more complex systems are not dealt with as their formulation is still in the initial stages and they are of insufficient generality.

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