

# THEORY OF ELECTRIC POLARIZATION

C. J. F. BÖTTCHER

VOLUME I

Dielectrics in static fields

# THEORY OF ELECTRIC POLARIZATION

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Second edition completely revised by

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**VOLUME I**

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## FOREWORD

As it is customary that an author of my age revises his own book, I should begin this foreword with an apologetic explanation. Having accepted the presidency of the Science Policy Council of The Netherlands, when the government founded this advisory body in 1966, I soon realized that this function did not leave sufficient spare time for the thorough revision of a scientific book. Fortunately the three main co-workers in my research unit at Leiden University kindly offered to take on this task. I then decided that I should not try to interfere, so that the considerable adaptation which the text needed after twenty years has been entirely their work and their responsibility.

I would like to express my gratitude for what they have achieved and my hope that the revised edition will be accorded a reception similar to that given to the first edition and its unchanged second printing.

C. J. F. Böttcher

## PREFACE TO THE SECOND EDITION

A period of twenty years is sufficiently long for a book to become outdated. In the case of dielectrics, the years between 1952 and the present have seen a great number of new developments, so that many subjects in the theory of electric polarization that are of great interest now, especially the dynamic behaviour of dielectrics, have not or insufficiently been dealt with in the 1952 edition of this book. Although a number of these subjects have been treated in monographs or books published since then, none of these books started from the same purposes as the first edition of "Theory of Electric Polarization", *i.e.*, a comprehensive treatment that can be used as a handbook as well as a textbook. In presenting a revised edition of this work, it was our aim to maintain this basic purpose, and to incorporate new material, thus giving an up-to-date and systematic treatment of the classical theory of dielectrics, in which much attention is paid to the fundamental concepts, and to the connection between theory and experimental results.

To prevent the increase of the book to an unmanageable size due to the large amount of new material, and to speed up the publication, we decided to split the book into two volumes. Volume I, the present volume, contains the theory of the static behaviour of dielectrics, and Volume II will contain the theory of the dynamic behaviour of dielectrics, as well as chapters on special subjects (determination of permanent dipole and multipole moments, polarization of solids).

In preparing the revised edition, not only additional material had to be incorporated. We also used the opportunity to make some changes in the order of presentation and to introduce a number of other improvements. Furthermore a historical introduction was added.

In the first volume of the revised edition the fundamental theory of electrostatics has been maintained as a starting-point. As in the first edition the Legendre polynomials and their value in solving potential problems have been treated extensively in Chapters I and II. The chapter on multipoles was reduced to one section in Chapter I, while the relation to the associated

Legendre polynomials was considered too much of a side track to keep it in this revised edition. Instead more attention has been paid to the problem of comparing multipole moments of molecules standardized according to different conventions. In the derivation of the relation between the electric field, the dielectric displacement, and the polarization, use has now been made of the concept of a dipole density.

The chapter on "Polarization and Energy" was placed directly behind the chapters on fundamental electrostatics, and more attention has been paid to the multipole terms in the electrostatic interaction energy between two molecules. Some material contained in this chapter in the first edition was postponed to Chapters IV, V and VII. The chapter "The Reaction Field" now contains a section on "Reaction Field and Energy"; more attention has been paid to the case of an ellipsoidal cavity.

The chapters on polar and non-polar dielectrics in static fields of the first edition were completely reorganized. The material has been split into a chapter "The Dielectric Constant in the Continuum Approach to the Environment of the Molecule" (Ch. V), and a chapter "Statistical-mechanical Theories of the Dielectric Constant" (Ch. VI). In both chapters polar as well as non-polar dielectrics are treated. In Chapter V the generalization of the continuum theory to the case of ellipsoidal cavities has been incorporated. Chapter VI contains new sections on dielectric virial coefficients and on the Kirkwood-Fröhlich equation; the application of this equation to polymers and to associating liquids is discussed in detail.

The developments in the field of non-linear dielectrics (*e.g.*, the so-called anomalous saturation effect) made it necessary to devote a new chapter to this subject (Ch. VII). In this chapter also the enlarged section on electrostriction has been incorporated.

As in the first edition the mathematics used in the book are reviewed shortly in a number of appendices; due to the revisions in the treatment of the multipoles the appendix on the associated Legendre polynomials could be abandoned. Because of these appendices the book can also be used by students with knowledge of elementary calculus and vector algebra only.

When used as a textbook for an advanced course in the theory of dielectrics it is convenient to leave out the sections dealing with ellipsoidal shapes (sections 9d, e, 20, 22, 30, 33) and to skip the small print everywhere. Furthermore section 5 (general multipoles) can be broken off after the definition of ideal multipoles. The Chapters IV and VII can be included at will, but it

should be noted that in Ch. VII only sections 41 (introduction), 42 (normal saturation), and 45 (electrostriction), are independent of the statistical-mechanical theory developed in Ch. VI.

For introductory courses in dielectrics we suggest the following sections and parts of sections: 1, 2, 3 up to application b, 6, 7, 8, 9a, b, c, 10, 11 up to and including eqn. (3.9), 17, 18, 19, 25, 26, 27, 28, 29, 31, 40 up to a, 41 up to eqn. (7.7).

Leiden, November 1972

O. C. van Belle  
P. Bordewijk  
A. Rip

## IMPORTANT SYMBOLS

*(The numbers indicate the page where the symbol is introduced)*

$a$	radius of sphere or spherical cavity, half of principal axis of ellipsoid
$A$	first virial coefficient, 231
$A$	affinity, 306
$A_n$	abbreviation of $(1 - n\alpha_1\alpha_2/s^6)$ or $(1 - n\alpha^2/r^6)$ , 121, 236
$A_\alpha$	$(\alpha = a, b, c)$ shape factor for ellipsoid, 79
$\mathbf{A}$	depolarizing tensor for ellipsoid <i>in vacuo</i> , 316
$\mathbf{A}$	3N-dimensional tensor connected with the polarizability of a system, 209
$\mathcal{A}$	first dielectric virial coefficient, 232
$\text{\AA}$	Ångstrom unit ( $10^{-8}$ cm)
$b$	half of principal axis of ellipsoid
$B$	second virial coefficient, 231
$\mathcal{B}$	second dielectric virial coefficient, 232
$c$	half of principal axis of ellipsoid
$C$	third virial coefficient, 231
$C$	proportionality constant of the Van der Waals attractive potential, 227
$C$	orthogonal transformation matrix, 263, 340
$\mathcal{C}$	third dielectric virial coefficient, 232
$d$	density
$D$	Debye unit ( $10^{-18}$ e.s.u. of electric moment), 11
$D$	dielectric displacement, 59
$e$	electric point charge, total positive charge, total charge, 9, 40



$e_0$	charge of electron, 11
$\mathbf{e}$	unit vector in the direction of the external field, 206
$\mathbf{e}$	3N-dimensional vector connected with the unit vector in the direction of the external field, 213
$\mathbf{E}$	electric field, 11, 59
$\mathbf{E}_0$	external field, 74
$\mathbf{E}_0$	homogeneous part of the Maxwell field in a dielectric, 293
$\mathbf{E}_c$	cavity field, 78, 81
$\mathbf{E}_d$	directing field, 161, 173
$\mathbf{E}_i$	internal field, 70, 161
$\mathbf{E}_l$	local field, 208
$\mathbf{E}_s$	field due to the surroundings of a molecule, 130
$\mathbf{E}_F$	Fröhlich field, 252, 299
$\mathbf{E}_L$	Lorentz field, 166
$\mathbf{E}_0$	3N-dimensional vector connected with the external field, 209
$\mathbf{E}_l$	3N-dimensional vector connected with the local field, 209
$f$	reaction field factor, 129, 134
$F$	free energy
$\mathbf{F}$	force
$\mathbf{F}$	reaction field tensor, 130, 139
$\tilde{F}$	transformed free energy, 306
$\mathcal{A}$	transformed free energy, 108
$g$	chemical potential, 306
$g$	radial distribution function, 218
$g$	Kirkwood correlation factor, 249, 258
$\tilde{G}$	transformed free enthalpy, 319
$h$	correction factor for molar polarization, 193
$\mathbf{i}$	unit vector in direction of the x-axis
$\mathbf{I}$	unit tensor
$\mathbf{I}$	3N-dimensional unit tensor, 209
$\mathbf{j}$	unit vector in direction of the y-axis

$k$	Boltzmann's constant
$\mathbf{k}$	unit vector in direction of the z-axis
$K$	equilibrium constant
$l, l$	distance
$L$	Langevin function
$\mathbf{L}$	depolarizing tensor, 80
$m$	dipole strength, 34
$m$	mass of microscopic particle, 60
$m$	electric moment, dipole moment, 9, 10
$\mathbf{m}$	3N-dimensional vector connected with the dipole moments of the molecules, 209
$M$	molecular weight
$M, M$	instantaneous dipole moment of a dielectric, 205
$M_d$	orientational part of the instantaneous dipole moment of a dielectric in Fröhlich's model, 251
$M_i^*$	average moment of a microscopic sphere with the central dipole held fixed, 246
$n$	refractive index, 2, 173
$n$	number of moles per $\text{cm}^3$ , molar density
$n_D$	refractive index for $\text{Na}_D$ -line
$\mathbf{n}$	unit vector in arbitrary direction
$\mathbf{n}$	unit vector normal to a surface
$N$	number of molecules in a system, 207
$N$	number of particles per $\text{cm}^3$ , number density, 131
$N_A$	Avogadro's number
$\mathcal{N}$	number of molecules in a microscopic sphere, 207
$p$	pressure
$p$	probability, weight function
$p$	induced molecular dipole moment, 109
$P_n$	Legendre polynomial, 25
$P_n^{(m)}$	associated Legendre polynomial, 58
$P$	dipole density, electric polarization, 22, 69
$P_{\text{in}}$	induced polarization, 251

$P_{\text{or}}$	orientation polarization, 251
$P_{\alpha}$	induced polarization, 160
$P_{\mu}$	dipole polarization, 160
$\mathcal{P}$	electric polarization, 69
$[P]$	molar polarization, 170
$q$	quadrupole strength, 34, 45, 48
$q_0$	factor characterizing a quadrupole moment not leading to a potential contribution, 49
$Q_n$	Legendre polynomial of the second kind, 140
$Q$	quadrupole moment, 44
$Q'$	standardized quadrupole moment, 49
$Q_H$	quadrupole moment standardized according to Hirschfelder, 52
$Q_{\text{norm}}$	quadrupole moment standardized according to Buckingham, 51
$\varrho$	quadrupole density, 61, 69
$\partial Q$	amount of heat absorbed by a system
$r, r$	radius vector
$R$	gas constant
$R_s$	reduction factor of saturation, 304
$R$	reaction field, 129, 134
$s, s$	distance
$ds, ds$	differential line element
$S$	surface
$S$	entropy
$dS, dS$	differential surface element
$t$	temperature in centigrades
$T$	absolute temperature
$T$	torque
$T$	dipole field tensor, dipole-dipole interaction tensor, 18, 116
$T$	3N-dimensional tensor connected with the dipole-dipole interactions, 209
$u$	octupole strength, 45
$U$	internal energy, energy of a system

$U$	octupole moment, 44
$v$	volume
$dv$	differential volume element
$V$	potential energy
$V$	volume
$W$	work
$x$	molar fraction, 261
$y$	reaction coordinate, 306
$y^{(n)}$	$2^n$ -pole strength, 35
$Y^{(n)}$	$2^n$ -pole moment, 53
$z$	number of nearest neighbours of a molecule, 249
$\alpha$	polarizability, 86
$\alpha^e$	polarizability connected with electronic polarization, 173
$\alpha^a$	polarizability connected with atomic polarization, 191
$\alpha$	polarizability tensor, 87
$\beta$	compressibility, 319
$\beta_E$	electrocaloric coefficient, 103
$\beta$	first hyperpolarizability tensor, 290, 310
$\gamma$	second hyperpolarizability tensor, 290, 310
$\delta$	delta function, 352
$\delta_{ij}$	Kronecker delta, 341
$\epsilon$	dielectric constant, permittivity, 1, 71, 159
$\epsilon'$	ratio $D/E$ for non-linear dielectrics, 291
$\epsilon_0$	field independent part of the permittivity, 289
$\epsilon_\infty$	dielectric constant characteristic for the induced polarization, 172
$\epsilon_i$	internal dielectric constant, 88
$\epsilon_E$	incremental dielectric constant, 289

$\epsilon$	permittivity tensor, 71
$\Delta\epsilon$	electric saturation term, 290
$\Delta\epsilon_a$	anomalous saturation term, 303
$\Delta\epsilon_e$	saturation term due to electrostriction, 318
$\Theta$	permanent molecular quadrupole moment, 109
$\lambda$	heat of vaporization, 155
$\mu$	value of permanent molecular dipole moment, 109
$\mu_{\text{gas}}$	permanent moment calculated from measurements on diluted gases, 179
$\mu$	permanent molecular dipole moment, 109
$\mu^*$	permanent molecular dipole moment enlarged by the reaction field, 135
$\mu_d$	molecular dipole moment in Fröhlich's model, 251
$\mu_e$	external moment, 134
$\mu$	3N-dimensional vector connected with the permanent dipole moments, 209
$\nu$	stoichiometric coefficient, 306
$\xi$	coefficient of non-linear dielectric behaviour, electric saturation coefficient, 71, 289
$\xi$	tensor of non-linear dielectric behaviour, 289
$\rho$	volume charge density, 12
$\sigma$	surface charge density, 12
$\sigma$	diameter of rigid sphere, 227
$\phi$	potential of electric field, 13
$\varphi$	volume fraction, 200
$\varphi$	molar volume of a mixture, 261
$\chi$	dielectric susceptibility, 70
$\chi$	dielectric susceptibility tensor, 71
$\Omega$	permanent molecular octupole moment, 109

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## HISTORICAL INTRODUCTION

Electric polarization has long been a subject of investigation, different aspects being emphasized in different periods.

As a natural phenomenon, electricity was known in ancient times, but it was not until the eighteenth century that the first experimental studies were undertaken, making it possible to establish a clear distinction between positive and negative electric charges—as they were later called—and between conductors and insulators. It was discovered that large quantities of electric charge could be stored in a condenser, an apparatus consisting of two conducting plates separated by insulating materials. The condenser constructed in 1745 by Cunaeus and Musschenbroek<sup>1</sup> became very popular for a variety of experimental purposes under the name of Leyden jar.

Relatively little attention was paid to the properties of the insulating material until 1837, when Faraday<sup>2</sup> published the first numerical results of measurements on this material, which he called the dielectric. Cavendish<sup>3</sup> had performed comparable experiments about sixty years earlier, but his results remained unpublished until 1879.

The results of Faraday's rather crude measurements indicated that the capacity of a condenser was dependent on the nature of the material separating the conducting surfaces. For the ratio between the capacity of a condenser filled with a dielectric and the capacity of the same condenser when empty, Faraday introduced the term *specific inductive capacity*. This quantity is now generally called the permittivity or the dielectric constant, and denoted by  $\epsilon$ .

In this period, other electric and magnetic phenomena were also investigated intensively. The results were summarized by Maxwell<sup>4</sup> in the middle of the 1860s in his unified theory of electromagnetic phenomena. In this theory the permittivity is conceived to be the ratio between the electric field intensity and the dielectric displacement, introduced by this author. Since light was taken as a form of electromagnetic radiation, it followed that for most dielectrics the dielectric constant should be equal to the square of