

THEORY OF ELECTRIC POLARIZATION

C. J. F. BOTTCHER AND P. BORDEWIJK

VOLUME II
Dielectrics in time dependent fields

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PREFACE

For the preparation of the second volume of the revised edition of this book, the same aims were set as for the first volume, namely, to maintain the character of the book as a comprehensive treatment of the theory of dielectrics, making any additions and alterations necessary to bring the book up-to-date. Applied to the theory of dielectrics in time-dependent fields, the main subject of this volume, this led to rather drastic changes.

As a starting point, some fundamental aspects of dielectric behaviour in time-dependent fields, relevant to both orientational polarization and induced polarization, are treated in Chapter VIII. This chapter is an extension of sections 42, 43, and 45 in Chapter VIII of the first edition. Next, the behaviour of the orientational polarization in time-dependent fields is discussed. This subject was originally treated in one chapter (Ch. X), but it has now been given three chapters. Chapter IX covers the phenomenological theory of dielectric relaxation, with an extensive survey of the various descriptions suggested in the literature and a discussion of their practical applicability. The relationship between macroscopic dielectric relaxation behaviour and the dipole correlation function is considered in Chapter X, and Chapter XI treats the molecular theory of the dipole correlation function under various conditions. In the latter chapter, data from dielectric measurements are also compared with other data concerning the molecular reorientation, *e.g.* derived from nuclear magnetic relaxation and obtained with spectroscopic techniques.

The material discussed in the remaining sections of Chapter VIII of the first edition is now presented in Chapter XII, with the exception of section 50, which has been expanded to make a new chapter (Ch. XIII) on the Kerr effect and related phenomena. Chapter XIV deals with the determination of permanent dipole moments (originally treated in Chapter IX), with an added section on the determination of permanent quadrupoles. As in the first edition, the last chapter deals with solids, but with the emphasis now placed on the dielectric properties of solids; spontaneous polarization is discussed only briefly, but a section on the dielectric properties of liquid crystals has been added. Two

Appendices are also included in this volume, one concerning complex numbers and the other Laplace and Fourier transforms.

As a selection for a course on dielectric theory, we suggest the whole of Chapter VIII, sections 54, 55, and 57 of Chapter IX, section 64 of Chapter X, and Chapter XI, where sections 73–77 can be omitted or included independently. The choice of material from the remaining part of the book will depend on the specific purpose of the course.

In concluding this preface, I wish to thank the many individuals who contributed in one way or other to the realization of this volume. Of the few who can be mentioned by name, I shall begin with Dr. O. C. van Belle and Mr. A. Rip, with whom I shared the responsibility for the first volume and who contributed valuable criticism on the present volume. Mr. Rip also drafted section 64 and the Appendices. I am grateful, too, for many discussions with Dr. J. C. Leyte on infrared bandshape analysis and nuclear magnetic relaxation, which greatly benefited the exposition in sections 68, 71, and 81. Section 97 could not have been written adequately without the discussions on the dielectric properties of liquid crystals that I had with Dr. W. H. de Jeu (Eindhoven). Dr. J. H. P. Colpa (Amsterdam) contributed the calculation of the Lorentz tensors in Table 54, as well as very useful criticism generally. Mr. M. Kunst assisted in reading the proofs. Finally, thanks are due to the Department of Physical Chemistry of the University of Leiden, which made it possible for me to spend so much time on the preparation of this revised edition.

Leiden, August 1977

P. Bordewijk

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*** absorption coefficient, II 22
- A*** parameter characterizing anisotropy of moment of inertia for symmetric-top molecules, II 190
- A_λ*** ($\lambda = a, b, c$) shape factor for ellipsoid, I 79
- A*** depolarizing tensor for ellipsoid *in vacuo*, I 316, II 428
- A**** depolarizing tensor for ellipsoid in anisotropic dielectric, II 430
- A*** first dielectric virial coefficient, I 232
- A_R*** first refractometric virial coefficient, II 291
- A_k*** first Kerr constant virial coefficient, II 333
- A*** quadrupole polarizability, II 375
- A⁽³⁾*** octupole polarizability, II 436
- A*** 3N-dimensional tensor connected with the polarizability of a system, I 209, II 404

- b*** half of principal axis of ellipsoid
- b*** rate of temperature increase, II 127
- b*** distance between two nuclei, II 177
- B*** Kerr constant, II 315
- B*** magnetic induction
- B*** second dielectric virial coefficient, I 232
- B_R*** second refractometric virial coefficient, II 291
- B_k*** second Kerr constant virial coefficient, II 333
- B*** quadrupole polarizability, II 375
- B*** sum of dipole-dipole interaction tensors over a sphere, II 432

- c*** half of principal axis of ellipsoid
- c*** velocity of light

C, C^*	Cotton-Mouton constants, <i>II</i> 370
$[C]$	molar Cotton-Mouton constant, <i>II</i> 370
C	dipole correlation function, <i>II</i> 151, 169
C_n	correlation function for Legendre polynomial P_n , <i>II</i> 175
$C_{km}^{(n)}$	correlation function for generalized spherical harmonic $D_{km}^{(n)}$, <i>II</i> 174
C_J	correlation function for angular momentum, <i>II</i> 196
C_{rv}	correlation function of rotational velocity, <i>II</i> 263
C_v	vibrational correlation function, <i>II</i> 310
\mathcal{C}	third dielectric virial coefficient, <i>I</i> 232
C_R	third refractometric virial coefficient, <i>II</i> 291
C_k	third Kerr constant virial coefficient, <i>II</i> 333
C	quadrupole polarizability, <i>II</i> 375
d	density
D	subsidiary order parameter, <i>II</i> 460
$D_{km}^{(n)}$	generalized spherical harmonic, element of Wigner rotation matrix $D^{(n)}$, <i>II</i> 174
D	dielectric displacement, <i>I</i> 59
\hat{D}	complex dielectric displacement, <i>II</i> 12
\mathcal{D}	generalized dielectric displacement, <i>II</i> 17
D^{rot}	rotation-diffusion tensor, <i>II</i> 204
D^{rot}	rotation-diffusion constant
D_v	diffusion constant for free volume, <i>II</i> 227
D_d	diffusion constant for defects, <i>II</i> 231
e_0	elementary charge
e, e_{\parallel}	unit vector parallel to electric field, or to director
e_{\perp}	unit vector perpendicular to electric field, or to director
e	3N-dimensional vector connected with unit vector e , <i>I</i> 213
E_a	activation energy, <i>II</i> 118, 224
$E_{\beta}(\omega)$	average energy of oscillator with frequency ω , <i>II</i> 147
E	electric field, <i>I</i> 11, 59
\hat{E}	complex electric field, <i>II</i> 12
\mathcal{E}	strength of electric field of optical frequency
E'	intensity of electric field gradient, <i>II</i> 375
E_0	external field
E_c	cavity field, <i>I</i> 78, 81

E_1	local field, I 208
E_1^*	part of local field proportional with the external field, II 408
E_0	3N-dimensional vector connected with the external field, I 209
E_1	3N-dimensional vector connected with the local field, I 209
f	reaction field factor, I 129, 134
f	distribution function in phase space, II 142
f	distribution function of molecular orientations, II 217
$f_{A,B}$	pulse-response function of A as a response to B
f_D	pulse-response function of dielectric displacement, II 8
f_g	pulse-response function of generalized dielectric displacement, II 18
f_I	pulse-response function of current density, II 16
f_P	pulse-response function of polarization, II 8
f_P^{or}	pulse-response function of orientational polarization, II 9
f_{sph}	pulse-response function of electric moment of a sphere, II 26
F_D	step-response function of dielectric displacement, II 8
F_I	step-response function of current density, II 16
F_P	step-response function of polarization, II 6
F_P^{or}	step-response function of orientational polarization, II 9
${}_1F_1$	Kummer's hypergeometric series, II 192
F	reaction field tensor, I 130
\mathcal{F}	Fourier transform, II 520
g	Kirkwood correlation factor, I 249
g_2	correlation factor for second Legendre polynomial, II 346
g_k	weight factor of relaxation time τ_k , II 39
g	distribution function of relaxation times, II 39, of activation energies, II 120
g	magnetogyric-ratio tensor, II 418
G	logarithmic distribution function of relaxation times, II 45
G	microscopic correlation factor connected with Kerr effect, II 354
G	intensity of velocity gradient, II 379
G_a	free enthalpy of activation, II 224
h	Planck's constant
h	intensity function, II 55
h	correction factor for molar polarization, I 193

h^e	correction factor for molar refraction, II 292
H_a	activation enthalpy, II 225
H	magnetic field
\mathcal{H}	Hamiltonian, II 140
i	$(-1)^i$, II 493
I	Intensity of electromagnetic radiation, II 317
I	nuclear spin quantum number, II 177
I	current density
I	moment of inertia, II 183
I	unit tensor
I	3N-dimensional unit tensor
J	quantum number of angular momentum, II 392
J	angular momentum, II 184
k	Boltzmann's constant
k	absorption index, II 21
k	reaction constant, II 259
k	rate of reorientation, II 220
K	second quantum number for free rotation, II 392
K	probability function for molecular reorientation, II 172
K	Kerr constant, II 116
$[K]$	molar Kerr constant, II 316
$[K^{opt}]$	molar Kerr constant for optical inducing field, II 317
$[K_1]$	contribution to molar Kerr constant by permanent dipoles, II 321, 337
$[K_2]$	contribution to molar Kerr constant by anisotropy of the polarizabilities, II 321, 337
$[K_3]$	contribution to molar Kerr constant by first hyperpolarizabilities, II 321, 337
$[K_4]$	contribution to molar Kerr constant by second hyperpolarizabilities, II 321, 337
K_0	equilibrium constant, II 259
K_0	memory function of dipole correlation function, II 264
K_J	memory function of angular momentum, II 201
K	local field tensor, II 336, 405
K^e	local field tensor for electronic polarization, II 335

l	optical path, <i>II</i> 316
L	Liouville operator, <i>II</i> 140
L	angular momentum of electrons, <i>II</i> 417
L	Lorentz tensor, <i>II</i> 433
L	$3n$ -dimensional tensor connected with the Lorentz tensors for a crystal with n molecules in the unit cell, <i>II</i> 434
\mathcal{L}	Laplace transform, <i>II</i> 509
m	mass
m_e	mass of electron
m_p	mass of proton
m^*	generalized mass corresponding with reaction coordinate, <i>II</i> 223
m	electric moment of molecule, <i>I</i> 109, of a macroscopic body, <i>II</i> 26
m^m	magnetic moment of molecule, <i>II</i> 416
\mathbf{m}	$3N$ -dimensional vector connected with the molecular dipole moments, <i>I</i> 209.
M	molecular weight, average molecular weight, <i>II</i> 316
M	third quantum number for free rotation, <i>II</i> 393
M	electric moment of a system, <i>I</i> 207
M_1	sum of permanent dipole moments in a small sphere in a dielectric, <i>II</i> 152
n, n'	refractive index, <i>II</i> 21
\hat{n}	complex refractive index, <i>II</i> 21
n_∞^*	refractive index extrapolated to infinite wavelength, <i>II</i> 289
\mathbf{n}	unit vector normal to surface
N	number density
N'	reciprocal volume of unit cell, <i>II</i> 434
N_A	Avogadro's number
N	number of molecules in the system, <i>I</i> 207
\mathcal{N}	number of molecules in a small sphere in the system <i>I</i> 207
p	pressure
p	imaginary component of complex frequency, <i>II</i> 31
p	distribution parameter for Matsumoto-Higasi distribution, <i>II</i> 87
p_i	momentum conjugated with generalized coordinate q_i , <i>II</i> 140
p	induced moment of a molecule, <i>I</i> 109

- \mathbf{p} 3N-dimensional vector connected with induced moments, *II* 334
 P probability, *II* 227
 P_n Legendre polynomial, *I* 357
 \mathbf{P} electric polarization, *I* 22, 69
 $[P]$ molar polarization, *I* 170
 $[\bar{P}]_k$ apparent molar polarization of component k in a mixture, *II* 397
- q partition function, *II* 224
 q height of nematic potential, *II* 408
 q_i generalized coordinate, *II* 140
 Q numerical constant characterizing cubic lattice, *II* 407
 \mathbf{Q} quadrupole moment, *I* 44
- r polar coordinate, *I* 333, *II* 495
 r polarization index, *II* 180
 \mathbf{r} radius vector
 R gas constant
 R_K macroscopic correlation factor connected with Kerr effect, *II* 352
 $[R]$ molar refraction, *II* 290
 $[R_\infty^*]$ molar refraction extrapolated to infinite wavelength, *II* 291
- S unit-step function, *II* 6, 509
 S order parameter, *II* 458
 S_a activation entropy, *II* 224
- t time
 t temperature in centigrades
 T absolute temperature
 T_c clearing point, *II* 459
 T_1 nuclear magnetic relaxation time, *II* 176
 T torque
 T magnitude of torque
 T dipole-dipole interaction tensor, *I* 18, 116
 \mathbf{T} 3N-dimensional tensor connected with the dipole-dipole interactions, *II* 209
- \mathbf{u} unit vector

U	energy of a system
U	octupole moment, <i>I</i> 44
v	volume
v	phase velocity of a travelling wave, <i>II</i> 21
V	molecular volume, <i>II</i> 206
V_a	activation volume, <i>II</i> 244
W	work, energy of a molecule
x	molar fraction, molar fraction of solute
$x(t)$	fraction of molecules not reorienting during time interval t , <i>II</i> 220
x^*	reaction coordinate, <i>II</i> 223
α	distribution parameter in Cole–Cole equation, <i>II</i> 62, Havriliak–Negami equation, <i>II</i> 72, Fuoss–Kirkwood description, <i>II</i> 76
α	degree of complexation, <i>II</i> 250
α_p	thermal expansion coefficient, <i>II</i> 293
α	polarizability
$\hat{\alpha}$	complex polarizability, <i>II</i> 26, 304
$\hat{\alpha}^*$	effective complex polarizability, <i>II</i> 306
α^*	polarizability connected with electronic polarization, <i>I</i> 173
α^*	polarizability connected with atomic polarization, <i>I</i> 191
α	polarizability tensor, <i>I</i> 87
α^*	effective polarizability tensor, <i>II</i> 343, 433
α	3N-dimensional tensor connected with the polarizabilities of the molecules, <i>II</i> 404
$\Delta\alpha$	anisotropy of the polarizability
β	distribution parameter in Cole–Davidson equation, <i>II</i> 67, Havriliak–Negami equation, <i>II</i> 72, Williams–Watts equation, <i>II</i> 80
β	collision frequency, <i>II</i> 197
β, β_T	isothermal compressibility, <i>I</i> 319
β	average first hyperpolarizability, <i>II</i> 324
β^*	average effective first hyperpolarizability, <i>II</i> 350
β	first hyperpolarizability, <i>I</i> 310, <i>II</i> 317
β^*	effective first hyperpolarizability, <i>II</i> 350

$\Delta\beta$	first hyperpolarizability anisotropy, <i>II</i> 324
γ	microscopic correlation function, <i>II</i> 152
γ	gyromagnetic ratio of a nucleus, <i>II</i> 177
γ_{∞}	limiting value of C_{∞} for free rotation, <i>II</i> 197
γ	average second hyperpolarizability, <i>II</i> 325
γ^*	average effective second hyperpolarizability, <i>II</i> 340
γ	second hyperpolarizability, <i>I</i> 310, <i>II</i> 317
Γ	gamma function, <i>II</i> 514
δ	delta function, <i>I</i> 352, <i>II</i> 510
δ	Kronecker delta, <i>I</i> 341
δ	phase difference between dielectric displacement and electric field, loss angle, <i>II</i> 2, 15
Δ_u	depolarization of the Rayleigh scattering for unpolarized incident light, <i>II</i> 323
Δ_v	depolarization of the Rayleigh scattering for vertically polarized incident light, <i>II</i> 323
ϵ	static dielectric constant, permittivity, <i>I</i> 1, 71, 159, <i>II</i> 1
ϵ'	frequency-dependent dielectric constant, <i>II</i> 3, 11
ϵ''	loss factor, <i>II</i> 3, 11
$\hat{\epsilon}$	complex dielectric constant, <i>II</i> 12
ϵ^*	apparent dielectric constant of a heterogeneous system, <i>II</i> 476
ϵ_{∞}	dielectric constant of induced polarization, <i>I</i> 172, <i>II</i> 9
ϵ	dielectric tensor, <i>I</i> 71, <i>II</i> 426
$\Delta\epsilon$	dielectric anisotropy, <i>II</i> 462
ζ	parameter for the angle of intersection at the low-frequency side of the Cole-Cole plot, <i>II</i> 51
η	viscosity
η	parameter for the angle of intersection at the high-frequency side of the Cole-Cole plot, <i>II</i> 51
$\hat{\eta}$	generalized complex dielectric constant, <i>II</i> 18
η	tensor accounting for the dependence of the polarizability on the magnetic field strength, <i>II</i> 371

- θ polar angle, I 333, Eulerian angle, II 171
- Q permanent quadrupole strength of a molecule
- Θ permanent electric quadrupole moment of a molecule, I 109
- Θ_{norm} permanent electric quadrupole moment of a molecule according to Buckingham, II 419
- κ extinction coefficient, II 22
- κ ratio between dielectric constant and dielectric constant of induced polarization, II 163
- κ anisotropy parameter of the polarizability, II 321
- κ^e anisotropy parameter of the electronic polarizability, II 321
- λ complex frequency, II 31
- λ wavelength
- λ_0 wavelength in vacuo
- μ complex magnetic permeability, II 20
- μ_n nuclear magnetic moment, II 177
- μ permanent dipole moment of a molecule, I 109
- μ^* effective dipole moment, dipole moment in solution, II 348, 395
- μ_d dipole moment enlarged due to induced polarization, I 251, II 465
- μ 3N-dimensional vector connected with the permanent dipole moments of the molecules, I 209
- π ratio between circumference and diameter of circle
- π differential polarizability, II 336
- π^e differential polarizability for field of optical frequency, II 317, 371, 376
- π 3N-dimensional tensor connected with the differential polarizabilities of the molecules, II 334
- Π 3N-dimensional tensor connected with the differential polarizability of the system, II 334
- ρ volume charge density
- σ electric conductivity
- σ standard deviation, II 83

τ	dielectric relaxation time, <i>II</i> 38
τ_0	characteristic dielectric relaxation time for distribution of relaxation times
τ_{av}^*	average microscopic relaxation time, <i>II</i> 163
τ^*	characteristic time of free rotation, <i>II</i> 392
τ_n	correlation time for Legendre polynomial of degree n , <i>II</i> 175
τ_j	correlation time of angular momentum, <i>II</i> 196
φ	polar angle, <i>I</i> 333, <i>II</i> 495, Eulerian angle, <i>II</i> 171
φ	molar volume
φ	volume fraction occupied by the molecules, <i>II</i> 293
φ_k	volume fraction of component k
ϕ	potential of electric field, <i>I</i> 13
ϕ	potential of complex electric field, <i>II</i> 23
Φ_{sph}	autocorrelation function of electric moment of a sphere, <i>II</i> 147
Φ_{sph}^{or}	autocorrelation function of orientational polarization of a sphere, <i>II</i> 150
χ	dielectric susceptibility, <i>I</i> 70
χ	magnetic susceptibility of a molecule, <i>II</i> 418
χ	magnetic susceptibility tensor of a molecule, <i>II</i> 370
χ^v	macroscopic magnetic susceptibility, <i>II</i> 461
$\Delta\chi^v$	anisotropy of macroscopic magnetic susceptibility, <i>II</i> 461
ψ	Eulerian angle, <i>II</i> 171
ω	angular frequency, <i>II</i> 2
ω	angular velocity, <i>II</i> 182
$d\Omega$	infinitesimal space angle

CONTENTS

Preface	v
Important symbols	xi
 Chapter VIII. Phenomenological theory of linear dielectrics in time-dependent fields	1
46. Introduction	1
47. The response functions	5
48. The complex dielectric constant	10
49. The complex dielectric constant and the complex conductivity	15
50. The complex refractive index	19
51. The use of the complex dielectric constant in problems with time-dependent field sources	23
52. The Kronig-Kramers relations	30
53. Resonance and relaxation	38
References	44
 Chapter IX. The empirical description of dielectric relaxation	45
54. Introduction	45
55. The Cole-Cole plot	48
56. Approximations for the distribution function	53
57. A single relaxation time	59
58. Generalized expressions for $\epsilon(\omega)$	61
59. Generalized expressions for $\epsilon''(\omega)$ and $F_p^{\text{or}}(t)$	75
60. Some simple distributions of relaxation times	83
61. Superpositions of distribution functions	88
62. Applicability of the empirical distributions	92
63. The temperature as a variable	118
References	128

Chapter X. The relationship between macroscopic and molecular dielectric relaxation behaviour	139
64. Statistical mechanics of linear dissipative systems and the relationship between response functions and correlation functions	139
65 The relationship between the macroscopic and the microscopic correlation function	150
66. Comparison between macroscopic and microscopic relaxation behaviour	161
References	166
Chapter XI. The dipole correlation function	169
67. Introduction	169
68. General aspects of molecular reorientation	171
69. Short-time expansions	181
70. Freely rotating molecules	190
71. Rotational diffusion	202
72. Reorientation by discrete jumps	218
73. Distributions of relaxation times	226
74. Internal reorientations	236
75. Associating liquids	249
76. High-frequency phenomena	260
77. Results obtained from computer simulations	272
References	277
Chapter XII. Polarization in the infrared and optical frequency range	285
78. Introduction	285
79. The extrapolation of the refractive index to infinite wavelength	287
80. The Lorenz-Lorentz equation and its corrections	290
81. Application of the internal field theory to i.g. bandshape analysis	303
References	311
Chapter XIII. The Kerr effect and related phenomena	315
82. Introduction	315
83. The Kerr effect in dilute gases	317
84. The Kerr effect in condensed systems	333
85. Electrically induced n.m.r. line splitting	357
86. Extensions of the Kerr effect	364