Advances in Dielectrics

Series Editor

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Aims and Scope

Broadband Dielectric Spectroscopy (BDS) has developed tremendously in the last decade. For dielectric measurements it is now state of the art to cover typically 8-10 decades in frequency and to carry out the experiments in a wide temperature and pressure range. In this way a wealth of fundamental studies in molecular physics became possible, e.g. the scaling of relaxation processes, the interplay between rotational and translational diffusion, charge transport in disordered systems, and molecular dynamics in the geometrical confinement of different dimensionality – to name but a few. BDS has also proven to be an indispensable tool in modern material science; it plays e.g. an essential role in the characterization of Liquid Crystals or Ionic Liquids and the design of low-loss dielectric materials.

It is the aim of "Advances in Dielectrics" to reflect this rapid progress with a series of monographs devoted to specialized topics.

Target Group

Solid state physicists, molecular physicists, material scientists, ferroelectric scientists, soft matter scientists, polymer scientists, electronic and electrical engineers.

Jacopo Parravicini
Editor

Fröhlich Entropy Estimation and Dielectric Calorimetry

A Flexible Investigation Technique for Condensed Matter

Springer

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Foreword

Herbert Fröhlich: Life and Work

Herbert Fröhlich was born on December 9, 1905 in Rexingen, a small town in the Black Forrest; he entered the University of Munich as an undergraduate in 1927. Guided by Arnold Sommerfeld, he obtained the doctoral degree “D. Phil” (for a thesis on the photoelectric effect in metals) after only 3 years without ever having taken an undergraduate degree! From his first post as private lecturer at the University of Freiburg, where he was responsible for introducing modern physics, he was dismissed because of the upcoming Nazi regime and left Germany in 1933 for Russia, to work (at Frenkel’s invitation), as a “Foreign Expert,” in Joffe’s Physico-Technical Institute in Leningrad (St. Petersburg), Russia. There, he became acquainted with current work on semiconductors, and included a discussion of them in his now famous book *Elektronentheorie der Metalle* (Springer, 1936), which for some years was the only textbook to contain a treatment of semiconductors. Later it proved very influential when the technological potential of these materials started to be appreciated, particularly in the USA, where it was reprinted (in the German original) in 1943. The political situation in Russia forced him to flee again, and in 1935, he joined Mott’s department at the University of Bristol, England. There, he remained until 1948, having advanced to the position of a Reader. Recommended by J. Chadwick, he took up the first Chair of Theoretical Physics at the University of Liverpool—a position he held until his retirement in 1973, after which he was Professor Emeritus from 1976 until his death on January 23, 1991, at the age of 85. Between 1973 and 1976, he was Professor of Solid State Electronics at the University of Salford, though he still maintained an office in Liverpool, so he spent a total of 43 years there.

Fröhlich was elected Fellow of the Royal Society in 1951 and awarded with the Max Planck Medal of the German Physical Society in 1972; he received numerous honorary degrees worldwide. From 1974 until his death, he was an external member of the Max Planck Institute for Solid State Physics, Stuttgart, where he regularly

Fig. 1 Herbert Fröhlich photographed at a conference in Prague (Czech Republic) in the mid-1980s. (Courtesy of Prof. F. Kremer)

spent extended visits, as he did also to many other parts of the world, lecturing and discussing physics.

Fröhlich made fundamental contributions to various fields of physics, as diverse as meson theory, the theory of superconductivity, and the theory of dielectrics. He was the first who suggested that electron-phonon interaction is the key to explain superconductivity and his concepts paved the way to the approach of Bardeen, Cooper, and Shrieffer introducing "Cooper pairs." His book *Theory of Dielectrics* was for a long time—besides Debye's *Polar Molecules*—the standard textbook book discussing the interaction of electric fields with matter. In his later years, he became interested in order and dynamics in biological systems and coherent excitations therein. This triggered a multitude of experimental activities which are summarized in two textbooks *Coherent Excitations in Biological systems* (Eds. H. Fröhlich and F. Kremer, Springer 1983) and *Biological Coherence and Response to External Stimuli* (Ed. H. Fröhlich, Springer 1988).

This novel volume of Advances in Dielectrics aims to describe H. Fröhlich's concepts on thermodynamics and dielectrics in detail and to present experiments where it was fruitfully applied.

Leipzig, Germany Friedrich Kremer
December 2025

Preface

This volume, entitled *Fröhlich Entropy Estimation and Dielectric Calorimetry* within the series Advances in Dielectrics, seeks to elucidate the features and implications of assessing variations in thermodynamic potentials as framed by classical Fröhlich thermodynamic theory. This experimental methodology, which so far has been developed predominantly through Fröhlich entropy estimation, constitutes a relatively simple and cheap procedure, which may be regarded as a viable alternative to more established and widely employed techniques.

Fröhlich's theory addresses the variations in thermodynamic parameters arising in an ideal dielectric material subjected to an external electric field. When this process is experimentally implemented and quantitatively assessed, this theory—under appropriate assumptions—enables the determination of thermodynamic quantities through dielectric quantities measured as functions of temperature. This framework thereby opens the way to various experimental advances, allowing a transition from conventional dielectric thermal analysis to the more specialized domain of *dielectric calorimetry*. In fact, among the thermodynamic variables altered by the presence of an electric field, the most significant is the variation of entropy, referred to as *Fröhlich entropy* from the name of H. Fröhlich, who first derived the relevant equations. When the imaginary component of the static dielectric function is negligible—namely, far from resonance conditions—Fröhlich entropy can be evaluated from the real part of the dielectric function. As emphasized by Fröhlich himself, this quantity may serve as a figure-of-merit for the degree of order within the physical system under consideration. Accordingly, when interpreted in this sense, the values of Fröhlich entropy obtained from experimental data provide valuable insights into the evolution of the investigated compound, particularly with respect to temperature dependence, phase behavior, stability, transitions, and order-disorder states and phenomena. Since the underlying assumptions of this approach are relatively weak, it can be applied to a wide range of physical systems, thereby serving as a valuable extension of standard dielectric measurement techniques, such as dielectric thermal analysis and spectroscopy. Indeed, *Fröhlich entropy estimation* has thus far been successfully employed across diverse areas of condensed matter physics, including dipolar and nematogenic liquids, dipolar glasses, organic molecular crystals and semiconductors, metallic nanoparticles, inorganic disordered ferroelectrics, as well as proteins and enzymes. This breadth of applications demonstrates that Fröhlich entropy estimation constitutes a reliable investigative tool, endowed with considerable potential that remains to be further exploited.

The structure of this volume is organized as follows. After a general introduction to the topic (chapter "Introduction: Dielectric Calorimetry and Fröhlich Entropy Estimation"), the fundamentals of classical dielectric thermodynamic theory and related applications are briefly presented, with particular emphasis on Fröhlich's contribution (chapter "Elements of Thermodynamics of Dielectrics and Basic Theory of Fröhlich Entropy"); the specific extension of this framework to anisotropic and nonlinear media is then addressed in chapter "Generalized Fröhlich Entropy: Anisotropic and Nonlinear Media". Subsequently, widely employed experimental techniques for analyzing the state of order are reviewed in chapter "Experimental Techniques to Investigate the State-of-Order in Condensed Matter", for the purpose of comparison. Chapter "Meaning and Applications of Fröhlich Entropy" examines the physical meaning of the Fröhlich entropy quantity, including a discussion of Fröhlich's interpretation and its relevance for experimental investigations. Finally, the practical application of Fröhlich entropy and theory to specific physical systems and conditions is explored, namely, metallic nanoparticles (chapter "Fröhlich Entropy of Nanoparticles: Investigation of Phases, Phase Transitions and Melting"), soft matter and extreme conditions (chapter "Fröhlich Entropy in Soft Matter and Extreme Conditions"), organic semiconductors (chapter "Dielectric Thermodynamics of Organic Semiconductors"), and ferroelectric perovskites (chapter "Order–Disorder Transitions of Ferroelectric Perovskites by Fröhlich Entropy Investigations").

The contributors to this collaborative book were selected from among researchers who have successfully applied this approach to investigations in condensed matter physics. It is my hope that the present work will encourage its broader adoption within the scientific community, thereby providing researchers with a versatile, rigorous, and powerful instrument of inquiry.

Sesto Fiorentino, Firenze, Italy — Jacopo Parravicini
December 2025

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Jacopo Parravicini

L. D.

Contents

Acronyms and Variables

ADPs	Atomic displacement parameters
BB	Bouchard and Brioli
BDS	Broadband dielectric spectroscopy
bR	Bacteriorhodopsin
c	Electrostriction coefficient
c_D	Heat of polarization
C_p	Heat capacity at constant pressure
C_v	Heat capacity at constant volume
d	Direct piezoelectric effect coefficient
d	Converse piezoelectric effect coefficient
D, D	Dielectric displacement field
DETA	Dielectric thermal analysis
DS	Diffuse scattering
DSC	Differential scanning calorimetry
DSE	Debye scattering equation
DTC	Differential thermal analysis
E, E	Electric field
EBSD	Electron backscatter diffraction
EDS	Dispersive X-ray spectroscopy
ER	Ergodic relaxor (phase)
f	Heat of deformation coefficient
F	Helmholtz free energy
F_E	Field-dependent Helmholtz free energy
F_0	Field-independent Helmholtz free energy
FD	Ferroelectric domain
FE	Fröhlich entropy
FR	Ferroelectric (phase)
FT	Fourier transform
G	Gibbs free energy
H	Enthalpy
HOMO	Highest occupied molecular orbital

I	Isotropic (phase)
K_B	Boltzmann constant
LUMO	Lowest unoccupied molecular orbital
N	Nematic (phase)
NEXAFS	Near-edge X-ray absorption fine structure
NR	Normal relaxor (phase)
NRM	Nuclear magnetic resonance
OMS	Organic molecular semiconductors
p	Pressure
$\mathbf{P}$, P	Density of polarization, polarization
P	Power
PAS	Positron annihilation spectroscopy
PDF	Pair distribution function
PE	Paraelectric phase
PND	Polar nanodomain
PNR	Polar nanoregions
q	Electrostriction coefficient
Q	Heat
RT	Room temperature
S	Entropy
s	Fröhlich entropy for unitary field
S_E	Fröhlich entropy
S_0	Field-independent entropy
SEM	Scanning electron microscopy
STM	Scanning tunneling microscopy
T	Temperature
T_B	Burns temperature
T_C	Curie-Weiss temperature
T_g	Glass transition temperature
TDS	Thermal diffuse scattering
TEM	Transmission electron microscopy
TEN	Tetracene
TG	Thermogravimetry
TGA	Thermogravimetric analysis
TL	Thermoluminescence
TM	Thermomagnetometry
TMA	Thermomechanical analysis
U	Internal energy
u_e	Density of electric energy
U_e	Electromagnetic energy
U_E	Field-dependent internal energy
U_0	Field-independent internal energy
v	Volume
WH	Williamson and Hall
XANES	X-ray absorption near edge structure

XAS X-ray absorption
XRD X-ray diffraction

4T α-quaterthiophene

α Thermal expansion coefficient
$\boldsymbol{\alpha}$ Thermal expansion coefficient
β Thermomechanical coefficient
γ_E Volumetric electrostriction
γ_p Pressure coefficient of polarization
$\boldsymbol{\varepsilon}$, ε Dielectric constant
ε_s Static dielectric constant
ε_0 Vacuum dielectric constant
$\boldsymbol{\eta}$ Strain tensor
κ_T Isothermal compressibility
$\mathbf{\Pi}$ Pyroelectric coefficient
$\boldsymbol{\sigma}$ Stress tensor
$\mathbf{\Sigma}$ Elasticity

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