

ABSORPTION AND DISPERSION OF ULTRASONIC WAVES

KARL F. HERZFELD and THEODORE A. LITOVITZ

Department of Physics
The Catholic University of America
Washington, D. C.

1959



ACADEMIC PRESS New York and London

Copyright ©, 1959, by Academic Press Inc.

ALL RIGHTS RESERVED

NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM,
BY PHOTOSTAT, MICROFILM, OR ANY OTHER MEANS,
WITHOUT WRITTEN PERMISSION FROM THE PUBLISHERS.

ACADEMIC PRESS INC.

111 FIFTH AVENUE
NEW YORK 3, N. Y.

United Kingdom Edition

Published by

ACADEMIC PRESS INC. (LONDON) LTD.

40 PALL MALL, LONDON SW 1

Library of Congress Catalog Card Number 59-7683

PRINTED IN THE UNITED STATES OF AMERICA

PREFACE

The field of ultrasonics has grown enormously in the last forty years; it has not only provided us with much insight into problems of basic physics but also has found a large number of industrial and biological-medical applications. One of the most important basic studies by ultrasonic waves is that of the structure of matter, in which respect ultrasonic spectroscopy has taken a place along with optical and X-ray spectroscopy.

There are several excellent books on ultrasonics but none is devoted exclusively to the molecular basis of ultrasonic absorption and dispersion, nor is their treatment of this subject very detailed. We are principally interested in the information which ultrasonics can give on certain molecular processes in liquids and gases, namely, on relaxation mechanisms associated with the rate of energy exchange and the rate of structural changes in the fluid. The connection between ultrasonic data, the theory of chemical reaction rates, and the theory of the gas, liquid, and glassy states is considered. This book is intended as a treatise on this particular aspect of ultrasonics. In style and content it is halfway between a textbook and a handbook. The theories are extensively developed and we have tried to give the experimental results as completely as possible, but only in so far as they give quantitative information on relaxation processes. Since we hope that the book will be useful to experimental and theoretical physicists and to physical chemists the presentation of the mathematical development is extensive.

In Section A we have given a connected story of the field, with almost no formulae, so that the reader may see which parts of the detailed treatment he may omit if his interest is restricted to part of the subject only.

Unpublished material is included in several sections. Moreover a number of investigations recently published were occasioned by the writing of this book.

There are some important sections which we had to omit, to avoid making the book even longer than it is: the properties of aqueous salt solutions, including sea water, the field of polymers, and ultrasonic propagation in solids. W. P. Mason has just published a book on the latter subject.

We wish to use this occasion to pay homage to two of our late colleagues who were masters in ultrasonics and whose names appear often in the book, namely, the Very Reverend Francis E. Fox, O.S.F.S., and J. C. Hubbard.

We wish also to thank the Princeton University Press and Dr. F. Rossini, editor, for the permission to reprint several pages from K. F. Herzfeld's article in the volume, *Thermodynamics and Physics of Matter*, to the Editors of the *Journal of the Acoustical Society of America* and the *Journal of Chemical Physics* for permission to reproduce several figures, and to the Staff of the Academic Press for their long-suffering patience and help.

Catholic University of America
Washington, D. C.

March 5, 1959

KARL F. HERZFELD
THEODORE A. LITOVITZ

NOTATION

- a Amplitude of de Broglie wave (Chapter VII)
A constant
Constant in van der Waals equation (Secs. 35, 40)
- a_0 Lattice distance (Secs. 89)
- a_{js} Coefficient in the transformation to normal coordinates (Sect. 65, 68)
- A Affinity (Secs. 31, 103)
Frequency factor (Secs. 55, 70)
A constant in the equation of state (Sec. 33)
Abbreviation for $\Delta C'/C_v(C_p - C')$ (Sec. 17)
Abbreviation for $(\mathfrak{V}_\infty^2 - \mathfrak{V}_0^2)/\mathfrak{V}_\infty^2$ (Secs. 18, 25)
A constant defined by $\alpha'/f^2 = A[\tau/(1 + \omega^2\tau^2)] + B$ (Secs. 97, 98, 118)
- A, A_j Quantities related to the virial (Sec. 88)
- A_{js} Certain collision integrals (Sec. 36)
- b A constant
A coefficient (Sec. 61)
Constant in van der Waals equation (Secs. 35, 40)
- b_2, b_3 Molecular constants (Burnett) (Sec. 47)
- b_{sj} A coefficient in the transformation to normal coordinates (Secs. 65, 68)
- B A constant in the equation of state (Sec. 33)
A constant in the absorption equation $\alpha'/f^2 = A[\tau/(1 + \omega^2\tau^2)] + B$ (Secs. 97, 98, 118)
Second virial coefficient (Sec. 35)
- B' $= B/RT$ (Sec. 35)
- c Velocity of light in a vacuum (Sec. 75)
A constant (Sec. 61)
- c_{js} A coefficient in the transformation to normal coordinates (Secs. 65, 68)
- c Specific heat per gram
- C Specific heat per mole, measured quasi-statically
- C' Specific heat of internal degrees of freedom, relaxing specific heat
- \bar{C} or C_∞ $= C - C'$, specific heat of external degrees of freedom, specific heat at infinite frequency, frozen specific heat

C	Sutherland constant (Secs. 36, 39)
d	Diameter of Pitot tube (Sec. 45) Diameter of hard molecule (Secs. 82, 84)
D	Diffusion constant (Secs. 31, 34, 41, 87) Symbol indicating material differentiation (Secs. 1, 2, 3, 6)
D_T	Coefficient of thermal diffusion (Sec. 41)
e	Electric charge (Sec. 9)
E	Energy (usually per mole) Young's modulus (Sec. 112)
E_j	Energy of state j (per mole)
E'	Relaxing energy Internal energy $= E_2 - E_1$, energy difference in a two-state system Activation energy
E^*	Energy of activated state
$[Eu]$	Eucken number
f	Frequency
f	Frequency factor (Sec. 92)
f	A function (Secs. 31, 60, 61)
f_0	Maxwell distribution function of velocities (Sec. 36)
F	A function (Secs. 60, 61)
F	A force (Sec. 9)
F	Free energy
F_j	Free energy of state j
F^*	Free energy of activated state
F'	$= F_2 - F_1$, free energy difference in two-state systems
F	Distribution function of molecular velocities (Sec. 36)
g	A constant (Secs. 42, 45) A constant used to idealize sound velocities (Sec. 33) Degeneracy or weight of a quantum state $= 4\pi^2 pl/h$ (Secs. 58, 61, 65)
$g(\tau)$	Normalized distribution function of shear relaxation times (Secs. 105, 108)
$g^{(2)}, g^{(3)}$	Molecular distribution functions in space (Sec. 87)
G	A function (Sec. 24)
G	Collision operator (Sec. 36)
G	$= G' + iG''$, complex shear modulus (Chapter XII)
G_∞	Shear modulus at infinite frequency
h	Planck's constant Thickness of a layer (Sec. 83)

A constant characterizing the forces in triatomic molecules
(Secs. 64, 66)

H	$= E + pV$, enthalpy or heat content
H_j	Enthalpy of state j
H'	$= H_2 - H_1$, difference of enthalpy in two-state system
H^*	Enthalpy of activated state
H	Hamiltonian
H'	Perturbating Hamiltonian, Perturbation function
	Interaction energy
\mathcal{I}	Sound intensity (Sec. 32)
I	Sound intensity
	Moment of inertia (Sec. 64)
j	An index
	Angular momentum quantum number of relative motion
J	Angular momentum quantum number of molecular rotation (Secs. 64, 69)
k	Boltzmann's constant
k', k''	Constants used in Sec. 42
$k(\tau)$	Normalized distribution function of compressional relaxation times (Secs. 105, 109)
k_{js}	Rate constant for transition from state j to state s
\bar{k}	Forward reaction rate constant
\bar{k}	Backward reaction rate constant
k''	A rate constant in the thermodynamic theory (Secs. 31, 103)
K or K_{equil}	Equilibrium constant
K	$= K' + iK''$ Complex compressional modulus, defined in Eqs. 104-4,6
K_0	Compressional modulus at low frequencies (quasi-static)
K_∞ or \bar{K}	Instantaneous or frozen compressional modulus
K_2	$= K_\infty - K_0$ Relaxational part of compressional modulus
K	Hooke's law force constant (Sec. 9)
l	Range of repulsive forces (Chapter VII)
l'	Range of repulsive forces (Secs. 56, 57, 58)
L	Distance of nuclei in diatomic molecule (Secs. 64, 66)
	Thickness of transition layer in shockwaves (Sec. 45)
	Characteristic length for change of shape of high intensity wave (Sec. 33)
L_1, L_2, L_3	Molecular distances (Sec. 90)
m	Molecular mass
\tilde{m}	$= m_1 m_2 / (m_1 + m_2)$, effective mass

M	Molecular weight
\tilde{M}	Effective molecular weight
M	$= M' + iM''$ Complex longitudinal modulus (defined in Eq. 104-16)
M_0	Low frequency (quasi-static) longitudinal modulus
M_∞	$= K_\infty + \frac{4}{3}G_\infty$ Instantaneous (frozen) longitudinal modulus
n	Refractive index (Sec. 9)
	Number of particles (Sec. 19)
	Total number of moles (Sec. 27)
	Number of particles per unit volume
N	Number of particles
	Number of particles per unit volume (Secs. 9, 36, 40, Chapter X)
\tilde{N}	Number of molecules in first neighboring shell (Sec. 86)
N_A	Avogadro number
N_j	Normalization factor (Sec. 64)
p	$= -\frac{1}{3}(P_{11} + P_{22} + P_{33})$, hydrostatic pressure
\hat{p}	$= mw$ Linear momentum (in Chapter VII only)
$P - P_0$	Excess pressure in high intensity soundwave (Sec. 33)
P	Probability (Sec. 32)
P_{ij}	Stress component
P_{ij}'	$= P_{ij} + p$, deviatoric normal stress
P_{ij}'	$= P_{ij}$, $i \neq j$
P_{ij}''	Normal stress due to volume viscosity
[Pr]	Prandtl number (defined in Eq. 7-20)
q_s	Normal coordinates (Sec. 65)
q	$= 4\pi pl/h$ (Sec. 61)
Q	A molecular quantity (Sec. 36)
	Partition function (Secs. 92, 100)
	Scattering cross section (Secs. 61, 62, 69)
r	Number of rotational degrees of freedom (Secs. 34, 38)
	Distance
	Radius of a tube (Sec. 42)
	Reflection coefficient of amplitude of shear wave (Sec. 108)
r_0	Constant in Lennard-Jones formula
R	Universal gas constant
	Distance of molecule from center of cell (Sec. 86)
	Real part of propagation impedance for longitudinal waves, defined in Eqs. (104-32, 33)
R_s	Real part of propagation impedance for shear wave, defined in Eqs. 108-12, 14

[Re]	$= \rho \mathfrak{B}_0^2 / \eta \omega$ Reynolds number (Secs. 7, 47)
s_{ij}	Strain component
s	$= (\rho - \rho_0) / \rho_0 = -\frac{1}{3} (s_{11} + s_{22} + s_{33})$, condensation, defined in Eq. (3-1)
s_{ij}'	$= s_{ij} + s$, deviatory strain component, defined in Eq. (104-3)
s_{ij}	$= s_{ij}$, $i \neq j$, deviatory strain component, defined in Eq. (104-3)
s	As subscript, solvent (Sec. 29)
	As subscript, shear
	As subscript, running index
S	Entropy
S_j	Entropy of state j
S'	$= S_2 - S_1$ Entropy difference between two states
S^*	Entropy of activated state
S	As subscript means adiabatic or at constant entropy
S	An expression used to "reduce" measurements on shear waves (Secs. 108, 109)
t	Time
T	Temperature (Kelvin)
T_{tr}	Temperature of external (translational) degrees of freedom
T'	Temperature of internal (or relaxing) degrees of freedom
T_{rev}	Temperature at the end of a reversible process (Sec. 30)
$T_{ijij}^{(4)}$	A stress tensor (Sec. 88)
u	Velocity of jet (Sec. 45)
u_1, u_2, u_3	Components of flow velocity
U	Relaxing variable (Sec. 9)
	Real part of C_{eff} (Sec. 21)
U_s	Components of unit vectors occurring in Sec. 24
v	Arbitrary volume
v_f	Free volume (Sec. 85)
v_i	Volume element j , of size v' (Sec. 88)
V	Mole volume
V_a	Available volume (Sec. 84)
V_j	Mole volume of state j
V'	$= V_2 - V_1$, volume difference between states (2) and (1)
	Volume of one mole of holes (Sec. 91)
\mathfrak{B}	Sound velocity
w	Macroscopic flow velocity
	Molecular velocity (Chapter VII) (W is used in Sec. 62)
	Work (Sec. 32)
w_1, w_2, w_3	Components of macroscopic flow velocity

W_1, W_2, W_3	Components of molecular velocity
iW	Imaginary part of C_{eff} (Sec. 21)
x_1, x_2, x_3	Cartesian coordinates
x, y, z	Cartesian coordinates
x	A variable (Secs. 12, 15)
	Abbreviation for $i\omega$ (Sec. 21) or $-i\omega$ (Sec. 24)
x_i	$= n_i / \Sigma n_s$, mole fraction of component i
x	$= n_2 / (n_2 + n_1)$, mole fraction of component (2) in a system of two components only
\bar{x}	Mole fraction, calculated in moles of the monomer
X_i	Component of displacement in the direction x_i (Secs. 104, 108)
X_s	Components of unit vectors occurring in Sec. 24
X	An expression defined in Sec. 21
	A mole fraction (Sec. 40)
	Amplitude of vibration (Chapter VII)
	Reactance appearing in the propagation of longitudinal waves, defined in Eq. (104-32, 34)
X_s	Reactance appearing in the propagation of shear waves, defined in Eqs. (108-12, 13)
y	Cartesian coordinate
	A variable (Secs. 12, 15, 21)
Y_s	Components of unit vectors occurring in Sec. 21
$Y(2,2)$	A function (Sec. 62)
z	Cartesian coordinate
Z	$= \tau / \tau_c$, (nearly equal to) average number of collisions necessary for energy transfer
Z	$= R + iX$ Complex longitudinal impedance, defined in Eq. (104-31)
Z_s	$= R_s + iX_s$ Complex shear impedance, defined in Eq. (108-12)
α	Absorption coefficient of amplitude, in Centimeters ⁻¹
α_{class}	Classical absorption, defined in Eq. (7-17)
α'	$= \alpha - \alpha_{\text{class}}$, molecular absorption
β or β_0	Quasi-static coefficient of thermal expansion
$\tilde{\beta}$ or β_∞	Instantaneous or frozen coefficient of thermal expansion
β'	$= \beta - \tilde{\beta}$, relaxing part of thermal expansion coefficient
γ	$= C_p / C_v$
γ_∞ or $\tilde{\gamma}$	Instantaneous (frozen) value of γ
Γ	Angle between the molecular axis and the line of approach of a hitting atom (Secs. 64, 69)

δ	A small number
	A small angle
	A symbol for variation
Δ	$= C_p - C_v$, difference of specific heats
Δf	Shift in frequency (Sec. 52)
ΔF	Change of free energy in a reaction (Sec. 27, 28)
	Free energy of activation (Sec. 105)
ΔH	Heat of evaporation
Δr	Amplitude of vibration (Sec. 65)
ΔT	Fluctuation of temperature (Sec. 88)
$\Delta x, \Delta y, \Delta z$	Components of atomic vibration (Sec. 65)
$\Delta \rho$	Fluctuation of density (Sec. 88)
ε	Depth of the potential well in the Lennard Jones formula, defined in Eq. (59-2)
ε_j	Energy of quantum state j
ε'	An energy occurring in the expression for energy transfer, defined in Eq. (56-6')
ε	$= \varepsilon' - i\varepsilon''$, complex dielectric constant (Sec. 114)
ζ	Brownian motion constant (Sec. 87)
η, η'	Phase factors (Sec. 61)
η	Shear viscosity
η'	Volume, bulk or second viscosity
ϑ	Polar angle
ϑ	$= h\nu/k$, characteristic temperature of molecular vibration, defined in Eq. (58-9)
ϑ'	$= 0.815 \bar{M} \vartheta^{2/3}$, a temperature characteristic of the transfer of energy from vibration to translation, defined in Eq. (58-9')
ϑ_r	A temperature characterizing a rotational energy change, defined by Eq. (69-5)
κ or κ_0	Quasi-static or low frequency compressibility
κ_T or $(\kappa_T)_0$	Isothermal quasi-static compressibility
κ_S or $(\kappa_S)_0$	Adiabatic quasi-static compressibility
$\bar{\kappa}$ or κ_∞	Instantaneous or frozen compressibility
$\bar{\kappa}_T, \bar{\kappa}_S$	Isothermal and adiabatic instantaneous compressibility
κ'	$= \kappa - \bar{\kappa}$, relaxing part of compressibility
λ	Coefficient of heat conduction (Secs. 7, 34)
	Wave length of sound
λ_0	Wave length of light (Sec. 75)
Λ	Mean free path (Secs. 36, 83)
	A constant used in Sec. 69, defined in Eq. (69-3)

μ	$= \partial A / \partial n$, chemical potential (Sec. 31)
	Cosine of polar angle (Sec. 60)
ν	Frequency of molecular vibration
$\tilde{\nu}$	$= \nu / c = 1 / \lambda_0$, wave number of molecular vibration
ξ	Degree of advancement of a reaction defined in Eq. (27-5), generalized in Eq. (31-2)
Π	Indicates a product
ρ	Density
ρ_0	Undisturbed density
$\rho^{(1)}, \rho^{(2)}, \rho^{(3)}$	Probability functions (Sec. 87)
σ	Reciprocal of partition function for angular motion and rotation (Secs. 62, 64)
τ	Relaxation time
τ_c	Time between collisions, defined by Eqs. (36-2, 36-3)
τ_L	$= 4/3 \eta / \rho \mathfrak{B}_0^2$, Lucas time, defined in Eq. (7-9)
τ_L'	$= (4/3 \eta + \eta') / \rho \mathfrak{B}_0^2$, modified Lucas time, defined in Eq. (7-9')
τ_p	Relaxation time at constant pressure
τ_{Sp}	Relaxation time at constant pressure and entropy
τ_v	Relaxation time at constant volume
τ_s	Relaxation time for s'th process
τ_s	Relaxation time for shear
τ', τ'', τ'''	Times proportional to τ occurring in different expressions; see Sec. 18
τ^*	An apparent relaxation time defined in Chapter XII by the equation $\alpha' / f^2 = A \tau^* (1 + \omega^2 \tau^{*2}) + B$
φ	Angle
φ, φ'	Phase angle (Secs. 11, 16)
φ	A function (Sec. 39)
	A function of composition in chemical reaction (Secs. 27, 28, 29, 31)
Φ	A function describing deviation from Maxwell's distribution law (Sec. 36)
χ	An angle
$\psi^{(0)}, \psi^{(2)}$	Perturbations in the distribution function g (Sec. 87)
ψ^A	Translational wave function
ψ^{BC}	Vibrational wave function
ψ_i	Rotational wave function
Ψ	Total wave function
ω	$= 2\pi /$, circular frequency
$d\Omega$	Element of steric angle

Chapter VII

CONTENTS

Preface	v
List of Notations	xi
Introduction	1

A. GENERAL THEORY OF RELAXATION IN FLUIDS

I. The Stokes-Navier Equations of Hydrodynamics

1. The State of the Fluid	25
2. The Equations of Motion	27
3. The Linearized Hydrodynamic Equations	28
4. Thermodynamic Discussion of the Compressibility	30
5. The Linearized Wave Equation for a Nonviscous Fluid	32
6. Viscosity	34
7. The Stokes-Navier Equation. "Classical" Sound Absorption	38
8. Formal Introduction of Volume Viscosity	47

II. General Considerations on Relaxation

9. General Discussion of Resonance and Relaxation Phenomena	49
10. Energy Exchange between Internal and External Degrees of Freedom as Relaxation Phenomenon	55
11. The Effect of Slow Energy Exchange on Sound Propagation	59
12. Discussion of the Dispersion Equation	63
13. Different Ways of Evaluating the Dispersion Curve	67
14. The Absorption Curve	70
15. Continuation of the Discussion of Absorption	72
16. Continuation of the Discussion of Absorption and Dispersion: Kneser's Expression. Calculation of C_{eff}	76
17. Exact Calculation of Absorption and Dispersion	78
18. Dependence on τ . Summary of Characteristic Times	80
19. Exchange of Energy and Relaxation Equation	83
20. General Discussion of the Case in Which More Than One Relaxation Time Exists	90
21. The Excitation of Different Degrees of Freedom Which Behave like a Group of Parallel Reactions	93
22. Excitations of Different Degrees of Freedom Which Behave like Chemical Reactions in Series. Classical Theory	105
23. Excitation in Series, with Exchange with Translational Energy (Quantum Theory)	110
24. The Solution of the General Equations of Excitation in Series	117

25. Relation of Dispersion and Absorption if More Than One Relaxation Time Is Present. General Shape of the Curves	130
26. Mixtures	136
27. The Effect of Chemical Reactions	138
28. Discussion of Special Cases. Various Orders of the Reaction	143
29. Continuation of Discussion. Different Values of V' and H'	147
30. Does the "Volume Viscosity" Provide Actual Stresses, Even if the Relaxation Phenomenon is the Slow Energy Exchange with Internal Degrees of Freedom or a Chemical Reaction?	156
31. Thermodynamic Theory of Relaxation	159

III. Special Topics

32. Scattering	171
33. Absorption of High Intensity Sound Waves	174

B. GASES

IV. Application of the General Formulas to Gases

34. Application of Previous Equations to Ideal Gases	185
35. Correction for Nonideality of the Gas	188
36. Viscosity and Relaxation Time for Translational Energy	194
37. Assumption That Only Binary Collisions are Effective	202
38. Low Frequency Absorption. Ratio of Relaxation Absorption to Classical Absorption at Maximum	203
39. Gas Mixtures	206
40. Triple Collisions in Pure Gases and in Mixtures	209
41. Additional Absorption in Mixtures	215

V. Experimental Methods to Determine Velocity and Absorption of Ultrasonic Waves in Gases

42. Methods for Low Frequencies	217
43. The Ultrasonic Interferometer	219
44. Miscellaneous Methods	224
45. Aerodynamical Methods	225
46. Direct Methods for Measuring Absorption and Relaxation Time	229

VI. Experimental Results in Molecules Without Electronic Excitation

47. Translational Relaxation in Monatomic Gases	231
48. Methods to Determine Rotational Relaxation Time	234
49. Results for Rotational Relaxation	236
50. Oxygen, Nitrogen, Air	241
51. Other Diatomic Molecules	244
52. Linear Triatomic Molecules	246
53. Nonlinear Triatomic Molecules and Four Atomic Molecules	253
54. Large Molecules	255

VII. Theory of Vibrational and Rotational Energy Exchange

55. Introductory Remarks	260
56. The Theory of Landau and Teller (Classical)	262
57. Fundamental Quantum Consideration	267
58. Inelastic Scattering for an Exponential Interaction Potential	274
59. Introduction of a Better Interaction Potential	278
60. Tridimensional Case	285
61. Discussion of Scattering	288
62. Conclusion of the Tridimensional Calculation	295
63. Some Numerical Data. Effect of Molecular Frequency on Low Frequency Absorption	300
64. Simultaneous Transitions in Rotational, Vibrational, and Translational Energy	303
65. Polyatomic Molecules. More Than One Vibrations Is Involved. Complex Collisions	315
66. Numerical Results for Diatomic and Linear Triatomic Molecules	321
67. Further Numerical Discussion of the Effect of Impurities, of Complex Collisions, and of Exact Resonance	328
68. Polyatomic Molecules: Methane and Chlorinated Methanes	331
69. Theory of Exchange of Rotational and Translational Energy	336
70. Energy Transfer and the Kinetics of Chemical Gas Reactions	342
71. Summary and Comparison of Theory and Experiment	348

C. LIQUIDS

VIII. General Review of Ultrasonic Absorption and Dispersion in Liquids

72. Classical Absorption	353
73. Absorption of Ultrasonic Waves in Liquids: The Situation in 1948. Pinkerton's Classification of Liquids	354
74. Developments Since 1948. Critical Review of Pinkerton's Classification	359
75. Velocity of Sound Waves of Ultrahigh Frequency (UHF)	361

IX. Experimental Methods to Determine Dispersion and Absorption of Ultrasonic Waves in Liquids

76. Methods for Low Frequencies	365
77. The Ultrasonic Interferometer	366
78. Pulse Methods	367
79. Mechanical Method: Radiation Pressure Measurements	368
80. Optical Methods	369

X. Review of Theories of Liquids

81. Introduction	371
----------------------------	-----

82. Connection with Internal Pressure. Theory of Jäger	372
83. Heat Produced by Friction. Number of Collisions	375
84. Cubic Cell Model. Available Volume	377
85. Spherical Cell Model. "Free Volume" According to Thermodynamics	379
86. Spherical Cell Model. The Motion Treated as Simple Harmonic Motion	381
87. The Distribution Function; Calculation of η and η'	383
88. The Relaxation Time of the Distribution. Green's Theory	385
89. Brillouin's Theory of Viscosity	393
90. Eyring's Theory of Viscosity	395
91. The Theory of Bulk Viscosity by Gierer and Wirtz	398
92. Theory of Relaxation Time. Theory of Absolute Reaction Rates	400

XI. Kneser Liquids

93. Discussion of Specific Heats in Nonassociated Organic Liquids with Molecules of Moderate Size	404
94. A Cooperative Theory of Relaxation Time for Kneser Liquids	405
95. Comparison of Relaxation Time in the Gaseous and Liquid States. Thermal Relaxation as due to Interaction between a Pair of Molecules	406
96. Temperature Dependence of the Absorption in Kneser Liquids	411
97. Carbon Disulfide CS_2	412
98. Relaxation due to Rotational Isomerism	417
99. Liquid Mixtures	425

XII. Associated Liquids and Liquids with High Viscosity

100. The Theory of Hall	428
101. Eucken's Theory of the Constitution of Water	432
102. The Effect of Pressure on Sound Absorption in Water	435
103. The Associated Liquids (Other than Water) and the Glassy State	439
104. Elastic Moduli of Liquids	446
105. Distribution of Relaxation Times	454
106. Absorption and Dispersion Measurements in Glycerol	457
107. Absorption and Dispersion in <i>n</i> -Propyl Alcohol	461
108. Transversal or Shear Waves in Liquids	466
109. Compressional Relaxation in Associated Liquids. Comparison with Shear Relaxation	475
110. Velocity Dispersion in Associated Liquids	479
111. Numerical Relationships Between the Moduli	483
112. The Temperature Dependence of Elastic Moduli of Liquids	486
113. The Origin of Volume Viscosity in Associated Liquids	490
114. The Relation of Ultrasonic and Dielectric Relaxation Times	498
115. Ultrasonic Hysteresis at High Frequencies	503
116. Dissociation of Dimers: Acetic and Propionic Acids	505
117. Mixtures Containing Associated Liquids	509
118. Effect of Pressure on Ultrasonic Relaxation in Liquids	512
Author Index	517
Subject Index	524

INTRODUCTION

All fluids absorb ultrasonic waves by a "classical" mechanism, namely, loss through shear viscosity and (with very few exceptions) heat conduction, and show a corresponding dispersion. In addition, however, fluids (with the exception of monatomic gases and perhaps monatomic liquids) have an additional, "molecular," absorption and dispersion. Tisza has shown that this can always be formally introduced into the hydrodynamic equations by a "bulk viscosity." The opinion has been expressed that with the introduction of a bulk viscosity the problem is reduced to the integration of the modified hydrodynamic equations of Stokes and Navier.

We take a different standpoint. The problem can be illustrated by an electrical analogy. One could say that the problem of dielectric polarization was solved by the introduction of a dielectric constant by Faraday and Maxwell, and the only task remaining is that of formally integrating Maxwell's equations containing the dielectric constant. Thousands of papers on dielectric properties testify that this is not so. Three important problems are attacked:

1. What is the mechanism of dielectric polarization?
2. How does the dielectric "constant" depend on frequency?
3. How is the numerical value of the dielectric constant determined by the structure of a particular substance, and how does it depend on temperature and pressure?

Exactly the same problems for ultrasonic waves form the substance of this book:

1. What is the molecular mechanism explaining the existence of bulk viscosity?
2. How does bulk viscosity depend on frequency?
3. How is the numerical value of the bulk viscosity determined by the structure of a particular substance, and how does it depend on temperature and pressure?

In amplification of point 2, it is shown in Sec. 108 and Chapter XII that even the shear viscosity (and with it the classical absorption) is not constant at very high frequency.