Nicholas W. Tschoegl

The Phenomenological Theory of Linear Viscoelastic Behavior

线性粘弹性行为唯象理论导引［英］

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An Introduction

With 227 Figures and 25 Tables

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The cover illustrations portray the fundamental subdivision of viscoelastic behavior into rheodictic and arrheodictic response. Somewhat whimsically, they represent, on the left, an uncrosslinked and, on the right, a crosslinked polymer. The strings of beads simulate polymer chains. The small figures are "Maxwell's Demons": imaginary sentient, intelligent beings of atomic dimensions. In the illustration on the right the chains form a three-dimensionally crosslinked network. If a Demon finds itself on any portion of any chain, it can reach any other point on the network simply by walking along. In the illustration on the left the chains do not form a network. Here, the Demon is forced to jump or climb from one chain to the next. A crosslinked network cannot exhibit steady-state flow: therefore, the behavior is arrheodictic. An uncrosslinked network can flow: hence, the response is rheodictic. Both illustrations also contain 'entanglements'. The Demon is puzzled: are these crosslinks or not? Can it walk across them?

Cover illustrations: Christopher A. Tschoegl

This book is dedicated in deep gratitude to
Sophie
without whom I would not have become a scientist,
and to those who made me one:
Alex, Eric, John and Thor

[Gott . . .]

Tu mir kein Wunder zulieb.
Gib deinen Gesetzen recht
die von Geschlecht zu Geschlecht
sichtbarer sind.

Das Stundenbuch
R.M. Rilke

Preface

One of the principal objects of theoretical research in any department of knowledge is to find the point of view from which the subject appears in its greatest simplicity.

J. Willard Gibbs

This book is an outgrowth of lectures I have given, on and off over some sixteen years, in graduate courses at the California Institute of Technology, and, in abbreviated form, elsewhere. It is, nevertheless, not meant to be a textbook. I have aimed at a full exposition of the phenomenological theory of linear viscoelastic behavior for the use of the practicing scientist or engineer as well as the academic teacher or student. The book is thus primarily a reference work.

In accord with the motto above, I have chosen to describe the theory of linear viscoelastic behavior through the use of the Laplace transformation. The treatment of linear time-dependent systems in terms of the Laplace transforms of the relations between the excitation and response variables has by now become commonplace in other fields. With some notable exceptions, it has not been widely used in viscoelasticity. I hope that the reader will find this approach useful.

Elementary calculus and the rudiments of complex variable theory is the basic mathematical apparatus required for a profitable use of this book. The elements of transformation calculus are summarized in an Appendix. It introduces the notation used in this book and serves as a convenient reference. It also contains a discussion of those special functions, the delta, step, slope, ramp, and gate functions, which are indispensable in the theory. The reader is advised to scan the Appendix before he sets out on the book itself. This will show him whether he feels comfortable with what he knows about transformation calculus. If he does not, he should read one or the other of the many texts on the subject.

The compass of the book is outlined on the pages entitled Scope which follow this Preface. As pointed out there, the linear theory of viscoelastic behavior is a specialized form of general linear response theory. The theory has much beauty owing to the symmetry resulting from the interchangeability of the variables which are considered excitation and response, respectively. I placed much emphasis on the development of this duality, sometimes at the risk of being repetitive. I did this because there are pitfalls in interchanging the excitation and response, and there is the tendency, all too prevalent, of arguing by analogy. This can easily lead to erroneous statements or equations. A further advantage of fully working out both sides of the theory, i.e. stating it in terms of *relaxation behavior* (response to strain) as well as in terms of *retardation (or creep) behavior* (response to stress) is that the book becomes a compendium in which most of the important relations are readily available. A quite detailed subject index should further aid this purpose. I attempted to include in it all those terms that the reader – in my idio-syncratic opinion – might be most likely to wish to look up. It is clearly impossible to do this so that it will satisfy everyone. My apologies if I slipped too often. Clearly, every occurrence of every term could not be referenced. Particularly with 'bread-and-butter' terms such as *behavior, excitation, model, response, viscoelastic, etc.*, I had to concentrate on listing primarily those occurrences which refer to matters I thought important. I hope I did not miss too many items that should have been included. The entries are fairly extensively cross-indexed to minimize irritating *'see-under . . .'*-s but I could not avoid these completely.

A list of symbols and an author index precede the subject index. The main body of the book is subdivided into eleven chapters and the Appendix. The various parts of the book are headed by one or more mottos. In addition there is also a prefatory quotation, a prologue and an epilogue. Notes and literary references to these follow the Appendix.

The chapters and the Appendix are divided into sections, and the latter are often further divided into subsections. In numbering these divisions, the chapter number is separated by a decimal point from the section number in the first, and the subsection number in the second, decimal position. The numbering of equations, figures, and tables begins anew with each section. The number is preceded by the chapter and section number and is separated from them by a dash. Thus, Eq. (8.2–5) is Equation 5 of Section 2 of Chapter 8.

When two equations are placed on the same line they are assigned the same number and are distinguished from each other in references by numerical subcripts appended to the equation number. The same device is used to distinguish portions of concatenated equations. Thus, when an equation takes the form

$$f(x) = g(x) = h(x) \qquad (1)$$

Equation $(1)_1$ refers to $f(x) = g(x)$. Equation $(1)_2$ may be $g(x) = h(x)$ or $f(x) = h(x)$. The context always makes clear which is meant.

In the interest of brevity certain abbreviations were used routinely. Thus, 'step strain' is simply short for 'strain as a step function of time'. Similary, 'harmonic stress excitation' stands for 'excitation consisting of a stress in the sinusoidal steady-state'. I trust that these shortcuts will be self-explanatory everywhere.

Each chapter contains several fully worked problems. These are collected at the end of the chapter for easier cross-referencing and to avoid interrupting the flow of the exposition. Many are essential to a full understanding of the theory. Others clarify or amplify mathematical details. Still others are designed to develop and test the manipulative skill of the reader.

References to the work of others, indicated by numbers in brackets, and compiled at the end of each chapter, have been used sparingly. I would have liked greatly to follow the historical development of the subject in detail. However, the book was long in writing and would have taken even longer if this kind of scholarly research had been added. Therefore, I made reference only to the earliest work whenever this seemed appropriate. Otherwise, the literature is referred to merely when I thought it necessary for the sake of further clarification or an extension of the text. This restraint applies equally to my own papers. I apologize to all that feel left out.

I have added, in footnotes, short biographical comments to the names (capitalized in the subject index) of the more often quoted scientists, physicists, mathematicians, and engineers where they are first mentioned in the text. The way foreign names are commonly pronounced by English speakers unfamiliar with the spelling conventions (and their aberrations) of foreign tongues is all too often horrifying to others. I have therefore tried to render these names in the footnotes by their nearest American English phonemes, indicating the accent by an underscore. I hope that I have not erred here myself too often. Concerning my own name, for those who care, the letter combination 'Tsch' should be pronounced as the 'Ch' in Churchill. As for the rest of the name, the pronounciation has been clarified by Professor R. B. Bird of the University of Wisconsin, in the limerick:*

An eminent linguist called Tschoegl
at an age when he barely could gurgle
knew Turkish and Frisian
and Old Indonesian
and that the German for birds is Vögel.

During the writing of this book I was more then once reminded of the bewildered cry for help of a young warrior during Hungary's struggle against the Turks: "törököt fogtam, de nem ereszt"–'I caught a Turk but he doesn't let go of me'. It is thus with pleasure and pride that I acknowledge the contributions made by many of my students and collaborators who have taken part in working out specific details, checking problems, and reading and correcting parts of the manuscript. I would like to mention particularly (and in alphabetical order) R. Bloch, W.V. Chang, R.E. Cohen, M. Cronshaw, D.G. Fesko, R.W. Fillers, Çiğdem Gürer, L. Heymans, K. Jud, W.K. Moonan, S.C. Sharda, G. Ward, and K. Yagii.

Heartfelt thanks go also to several of my colleagues at Caltech who helped me with specific problems. These are especially professors Tom Apostol, Paco Lagerstrom, Willem Luxembourg, Charles de Prima, and John Todd.

Much of Chap. 5 was written during my two months tenure of a visiting professorship at the Technische Hogeschool, Delft, The Netherlands. Chapters 6, 7, and 9 as well as several sections in other chapters were worked out during a six month stay at the Johannes Gutenberg University in Mainz, Federal Republic of Germany, as the recipient of a U.S. Senior Scientist Award from the Alexander von Humboldt Foundation. It is a pleasure to mention that this award, also called the Humboldt Prize, was instituted by the German Federal Government in recognition of aid received from the United States after World War II.

Further work was done during my tenure of a visiting professorship at the Eidgenössische Technische Hochschule in Zurich, Switzerland, and during two months spent at the Centre de Recherche sur les Macromolécules in Strasbourg, France. Chapters 10 and 11 were drafted largely during a stay of three months at Edvard Kardelj University in Ljubljana, Yugoslavia. My sincere thanks go to all

* Not to be outdone, I offer advice on the writing of Professor Bird's name as follows:

Another great linguist called Bird
by his friends was once overheard
to mutter: in Chinese
for my name the sign is
the same as for bird. How absurd!

those who made these stays possible, particularly professors Hermann Janeschitz-Kriegl, Erhard Fischer, Joachim Meissner, Henri Benoit, and Igor Emri.

Last but not least I wish to acknowledge the dedicated work of a succession of very able secretaries, particularly (and, this time, in chronological order) the late Mrs. Eileen Walsh-Finke, Mrs. Kim Engel, Mrs. Lorraine Peterson, Mrs. Helen Seguine, Mrs. Rita Mendelson.

A great deal is being said in this book about models. I though it appropriate, therefore, to append as a Prologue Jorge Luis Borge's delightful little piece *Del rigor en la sciencia,* dealing with mankind's original model, the map.

The Epilogue at the end of the text admirably expresses my own feelings at the completion of my labor of many years.

Pasadena, January 1989 Nicholas W. Tschoegl

Scope

Il concetto vi dissi. Or,
ascoltate com'egli è svolto.

Leoncavallo: I Pagliacci

This book is concerned with the phenomenological description of the behavior of materials when these are deformed mechanically. Its subject matter is therefore a particular aspect of the science of *rheology*, that branch of mechanics which deals with the deformation and flow of matter. Material behavior is governed by *rheological equations of state* or *constitutive equations*. A constitutive equation links a dynamic quantity, the *stress*, with a kinematic quantity, the *strain*, through one or more parameters or functions which represent the characteristic response of the material per unit volume regardless of size or shape. In dealing with material behavior we may be concerned primarily with one or the other of two complementary aspects of the constitutive equation. Thus, we may be interested primarily in the stress-strain relations taking the material properties as given, or we may be concerned primarily with the material properties and not with the particular stresses and strains to which a given body of matter is subjected. The prediction of stresses and strains resulting from the imposition of prescribed tractions and/or displacements on a material body is the subject of *stress analysis* and is discussed in texts on solid and fluid mechanics. In this book we shall be concerned with the alternative way of viewing the constitutive equation, that of *material behavior*. An example may make the distinction clearer. The extension of a rod and the deflection of a cantilever beam fashioned of the same material represent different stress analysis problems. Both deformations, however, depend on the same material property. For a purely elastic material this is simply its Young's modulus. The determination of the modulus from either deformation assumes the stress-strain relations to be known. Conversely, the prediction of the extension of the rod or the imposed force requires that the modulus be known. Clearly, material behavior and stress analysis cover complementary aspects of deformation and flow.

Material behavior is termed *viscoelastic* if the material stores part of the deformational energy elastically as potential energy, and dissipates the rest simultaneously through viscous forces. We shall distinguish the *theory of viscoelastic behavior* as a discipline concerned with material behavior, from the *theory of viscoelasticity* which is concerned with stress analysis problems involving materials that are neither purely viscous nor purely elastic.

The rheological properties of a viscoelastic material are time-dependent. Although, in principle, all real materials are viscoelastic, this property becomes most prominent when the time required for the full development of a response is comparable with the time scale of the experiment performed to elicit it. The condition is notably present in polymeric materials which are thus the viscoelastic materials *par excellence*. Although we shall deal here more specifically with the theory as developed for polymeric materials, most of it is applicable, *mutatis mutandis*, to other materials such as metals and ceramics, inasmuch as they exhibit viscoelastic behavior. Furthermore, the theory, with suitable modifications in notation, is applicable also to time-dependent material behavior other than rheological. In particular, the theory of dielectric behavior is quite closely related to that of viscoelastic behavior. The two theories have, in fact, developed in close parallel and allusions to this will be made several times.

The foregoing has served to clarify provisionally the meaning of the words *viscoelastic behavior* in the title of the book. This will be enlarged upon in Chap. 2. However, some further comments appear in order.

By *phenomenological theory* I mean that I have tried to formulate a general framework which, in principle, applies to all viscoelastic materials regardless of their molecular structure. The viscoelastic behavior of polymers in relation to their structure has been described in several excellent books (see, e.g. [1, 2]). Similar books exist in the field of metals (see e.g. [3]). These have generally made use, without developing it explicitly, of the underlying phenomenological theory.

Confining the discussions in this book to *linear* behavior restricts it to behavior in deformations which are small enough so that a doubling of the excitation will elicit twice the response from the material. This restriction results in very considerable simplification and allows formulation of the subject as a unified theory applicable to all aspects of deformation and flow within the limitation to linear response. Moreover, the theory thus becomes another branch of *general linear response theory*. This permits us to use results worked out in other fields of physics concerned with linear response (e.g., electric circuit theory, the most highly developed of all linear systems theories) by applying the appropriate analogies (cf. Chap. 3).

Another important restriction ist that viscoelastic behavior is discussed in this book under the assumption that the thermodynamic variables, temperature and pressure, are constant. Thus I am dealing here exclusively with isothermal and isobaric viscoelastic behavior. I hope to present a discussion of the effects of temperature and of pressure elsewhere at another time.

Finally, the word *Introduction* in the subtitle refers to the level of presentation. In accordance with my aims stated in the Preface, I have foregone mathematical rigor without, I hope, sacrificing precision and clarity. The emphasis is thus on an understanding of the structure of the theory as it is applied in practice. The reader wishing to go on to more exacting treatments is referred to the excellent axiomatic presentations of Gurtin and Sternberg [4], and of Leitman and Fischer [5].

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Prologue

Del rigor en la cienca

. . . En aquel Imperio, el Arte de la Cartografía logró tal Perfección que el Mapa de una sola Provincia ocupaba toda una Ciudad, y el Mapa del Imperio, toda una Provincia. Con el tiempo, estos Mapas Desmesurados no satisficieron y los Colegios de Cartógrafos levantaron un Mapa del Imperio, que tenía el Tamaño del Imperio y coincidía puntualmente con él. Menos Adictas al Estudio de la Cartografía, las Generaciones Siguientes entendieron que ese dilatado Mapa eta Inútil y no sin Impiedad lo entregaron a las Inclemencias del Sol y de los Inviernos. En los Desiertos del Oeste perduran despedazadas Ruinas del Mapa, habitadas por Animales y por Mendigos; en todo el País no hay otra reliquia de las Disciplinas Geográficas.

Of Exactitude in Science

. . . In that Empire, the craft of Cartography attained such Perfection that the Map of a Single province covered the space of an entire City, and the Map of the Empire itself an entire Province. In the course of Time, these Extensive maps were found somehow wanting, and so the College of Cartographers evolved a Map of the Empire that was of the same Scale as the Empire and that coincided with it point for point. Less attentive to the Study of Cartography, succeeding Generations came to judge a map of such Magnitude cumbersome, and, not without Irreverence, they abandoned it to the Rigours of sun and Rain. In the western Deserts, tattered Fragments of the Map are still to be found, Sheltering an occasional Beast or beggar; in the whole Nation, no other relic is left of the Discipline of Geography.

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