Effective Medium Theory

Principles and Applications

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FOREWORD

The great classical theories of elasticity and electromagnetism evolved up to the nineteenth century. They were developed largely as continuum theories. As such, these theories remain immensely successful in engineering applications to this day. The early scientists and engineers invoked the idea of atoms only in the most distant way, even though atoms were fundamental to chemistry and electrochemistry, which were emerging at about the same time. The pioneers at that time recognised implicitly that the underlying atomic structure need not get in the way of macroscopic descriptions.

The way that the atomic scale linked to the engineering scale was less obvious. Craftsmen, as well as engineers, recognised that any averaging depended on what process or property was involved. People who worked with wood had no doubt that the fibrous grain structure was important; people who worked with crystals realised that some properties depended on the underlying atomic arrangements. Those who, like Darcy Thompson, looked at the microstructure of bone, realised that there was an intermediate scale on which the properties of materials depended. It was much later, in the middle twentieth century, that ideas about dislocations helped to rationalise approaches to this mesoscopic scale for the mechanical properties of metals. What gradually became clear was that there were at least three scales at which modelling was appropriate: the continuum macroscopic scale of engineering, the atomic scale, and an intermediate, mesoscopic, scale at which microstructure is handled systematically.

Tuck Choy's book brings together the major ideas in one of the most important approaches to the mesoscopic scale. Effective medium theory is a systematic approach of very wide application. It draws on a number of linked ideas. One idea is that, within the continuum approaches, there is a systematic way to define an average medium, which replaces all the complexity of a tree, a bone, a polycrystalline diamond film, or a superconducting oxide ceramic. A related idea is that one could define an average medium within which some other action occurs. This has led to some of the density functional analogues of effective medium theory. These powerful ideas address major issues in real materials, which are frequently inhomogeneous and described by a structure which is only statistically defined.

The averaging methods and their generalisations can go beyond the prediction of properties. They can describe the evolution of this microstructure, such as the way in which dislocation structures develop. Averaging methods are, of course, not the only approaches to the mesoscopic scale. Some properties cannot be represented by an average, but have strong dependences on very local features. Brittle fracture is an example, as is the prediction of currents in ceramic

superconductors. In these cases, it is necessary to go to many realisations of the microstructure, and to average over the behaviour of this ensemble.

The range of mesoscopic methods, and of effective medium theories in particular, has not always been appreciated. Many of the treatments in the literature are special cases, considered only in isolation. What Tuck Choy has done is to draw together the important themes. He has extended the theory, especially to the area of superconducting systems and of time-dependent properties. Further, he has developed some powerful new variational theorems. So this book gives more than a comprehensive and systematic approach to an important class of methods. It looks foward to some of the challenges which these methods face, as new systems and applications emerge. Tuck Choy's analysis also provides some of the new ideas by which these challenges might be tackled.

Marshall Stoneham
October 1998

PREFACE

"Each generation must examine and think through again, from its own distinctive vantage point, the ideas that have shaped its understanding of the world."
Richard Tarnas, in *The passion of the western mind*

My main motivation for writing this book is to bring together in a single text an exposition of the basic principles and broad applications of effective medium theory (EMT). I have set myself the task of trying to form a cohesive text, suitable as a reference for experimentalists, as well as a graduate text (with a few problems) for theorists. At appropriate places, I have taken the liberty of including some of my own unpublished results and insights. This avoids excessive pedagogy and provides me with extra impetus during the course of this work. The range of applications of the EMT means that I do have to make selections. However, I hope to set out a clear formulation of EMT with a study of its limitations, and to explore extensions beyond one-body EMT. To provide a wider perspective, I have in Chapter 5 collected together a number of related theories that share the 'spirit' of EMT, such as the acclaimed density functional theories, and the final Chapter 6 is devoted to problems in a range of application areas; for example, magnetoresistance, granular superconductors, viscoelastic properties of suspensions, and so on. Unfortunately, much as I would have liked, I had to leave out any discussions of modern computer simulation/numerical techniques. This vast area has important contributions from other disciplines, such as microwave engineering, and would have required an entire manuscript on its own.

Finally, owing to the enormity of the literature on the subject, I wish to apologise beforehand if any worker feels that his or her own contributions to EMT have unintentionally been omitted. I would gratefully appreciate any feedback and suggestions, and endeavour to incorporate them when the time comes for a revision.

Many people helped with this book. I wish to thank Marshall Stoneham for encouragement over the years, and the late Rudolph Peierls, who unfortunately did not live to see its first draft. The memory of my early discussions with him was a constant source of inspiration. Special thanks also go to the reviewers of my final draft: Marshall Stoneham, Walter Kohn, Roger Elliott, Sam Edwards, Gaoyuan Wei, Mukunda Das, and others, whose feedback provided many useful improvements. Permission from both the authors and publishers of the original papers/books where some of the figures have been adapted is greatly acknowledged. I wish to thank my wife Debra Ziegeler, graduate student Aris Alexopoulos, and in particular Rob Blundell at OUP, without whose help, with

the usual chores, the project would still lie dormant. This book is especially dedicated to the memory of my father and, most recently, my mother, who both passed away before its completion.

T. C. Choy
April 1999

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ESSENTIALS

This chapter is devoted to the essentials. It will, in fact, lay down the framework which forms the theme for the whole book. Although there appears to be some chronological order in the discussions, our purpose is primarily to bring out the main ideas as originally developed by the early pioneers in the field and to re-examine the key assumptions, some of which may in fact be questioned or improved through modern advancements. For this reason we start the initial discussions with the Lorentz field in section 1.1, invented by its founder to provide a description of macroscopic fields in a media but later found to be the key idea behind the Clausius–Mossotti relation (section 1.2) . This provides the basis for the Maxwell–Garnett (MG) formula (section 1.3) which is the first traditional effective medium theory (EMT). Following on, we shall develop the Bruggeman theory (section 1.4) which has certain advantages, but also disadvantages, over the MG theory. This will be discussed and made explicit through various examples. In section 1.5 a modern Green's functions formulation will be used to redevelop the two theories, which has important advantages for further improvements, particularly for the extension of the theories to higher orders. This will also lend itself naturally to the ideas in the later chapters where we shall contrast the static and dynamical versions of the EMT, and the problems associated with them. The chapter concludes in section 1.6 with a summary list of tables of equivalent problems and other applications of the theory for later reference. The example problems are especially designed to highlight certain features and limitations of the theory.

1.1   The Lorentz field

We begin our study by deriving one of the central concepts in this book, the well known Lorentz local field relation, which is a subject treated in many textbooks on solid state physics and electromagnetism; e.g. Kittel (1971), Ashcroft and Mermin (1976), and Reitz and Milford (1970). Originally the idea was invented by Lorentz (1870), as part of his programme to develop macroscopic electrodynamics (see, for example, Jackson 1975). In Lorentz's treatment, Maxwell's equations first operate at the microscopic level in terms of the electromagnetic fields $\mathbf{E}$ and $\mathbf{B}$, which obviously vary in space and time on microscopic scales. By a suitable averaging process, we arrive at the macroscopic Maxwell equations involving both $\mathbf{E}$, $\mathbf{B}$ and the derived fields $\mathbf{D}$ and $\mathbf{H}$ which include all polarisation

effects due to the medium; see, for example, Van Vleck (1932).[1] It also appears that Lorentz had the idea that there should be considerable flexibility in defining this averaging process. Indeed (see, for example, Ashcroft and Mermin 1976), the form of the averaging function is expected to be irrelevant as long as it is smooth over molecular dimensions and timescales. In the modern context this point has not been sufficiently re-examined.[2] We now know that there are at least three levels in which the physics differ. These are the microscopic, the mesoscopic and the macroscopic. It is forseeable that at the mesoscopic level some essential modifications to Lorentz's idea may be necessary. The macroscopic Maxwell equations thus derived, whose forms are independent of the material media, are however incomplete. In addition, Lorentz's exposition can only be deemed complete if the corresponding constitutive relations: $\mathbf{D} = \mathbf{D}(\mathbf{E}, \mathbf{B}), \mathbf{H} = \mathbf{H}(\mathbf{E}, \mathbf{B})$ are both specified. This step depends notably on the material media. The displacement field $\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P}$ and magnetic field $\mathbf{H} = \mathbf{B} - 4\pi\mathbf{M}$, to linear orders, is valid only when quadrupole and higher order multipole polarisation fields are ignored. They consist of the external field plus a supplement coming from the polarisable entities which constitute the media. These polarisation fields are denoted by $\mathbf{P}$ and $\mathbf{M}$ respectively. In addition, for conducting media, there is a constitutive relation $\mathbf{J} = \mathbf{J}(\mathbf{E}, \mathbf{B})$, again, Ohm's law: $\mathbf{J} = \sigma\mathbf{E}$ being only the linear case. Here σ can also depend on the $\mathbf{B}$ field if there exists a magnetoresistance. It is for the purpose of establishing these constitutive relations that the concept of the Lorentz field was invented. Without loss of generality, we shall specialise to the case of molecular dipoles arranged on a regular (cubic) lattice. Lorentz's assumption is that the local field $\mathbf{E}_{loc}$ experienced by a molecule is not the macroscopically averaged $\mathbf{E}$ field but, instead, $\mathbf{E}_{loc}$. This consists of the electric field produced by all external sources *and* by the polarised molecules in the system, *except* for the one molecule at the point in question. In fact, we must remember that the macroscopic field $\mathbf{E}$, by definition, is the force on an infinitesimal unit test charge in the dielectric that is small and thus unable to disturb the charge distribution in the media, but is large by molecular dimensions. To evaluate the local field, a spherical cavity which is macroscopically small but microscopically large is defined around the given molecule. The argument follows by noting that, from Fig. 1.1, we can replace the dielectric outside the cavity by a system of bound charges. Hence

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[1] Evidently some care has to be exercised here. In general, the spatial average has to be over dimensions of at least several lattice spacings and temporal averages must be longer than all molecular times. It is perhaps noteworthy that, in a vacuum, the derived fields $\mathbf{D}$ and $\mathbf{H}$ are one and the same with the fields $\mathbf{E}$ and $\mathbf{B}$ respectively, when using Gaussian units $\epsilon = \mu = 1$, which is slightly advantageous. Henceforth we shall adhere to Gaussian units. A conversion table for electromagnetic units can be found, for example, in the Appendix section of Jackson (1975).

[2] In fact there are difficulties here, as it can be shown, via a suitable choice of gauge, that the $\mathbf{D}$ and $\mathbf{H}$ fields are redundant; thereby questioning the physical content of Lorentz's averaging procedure (Yan 1995).
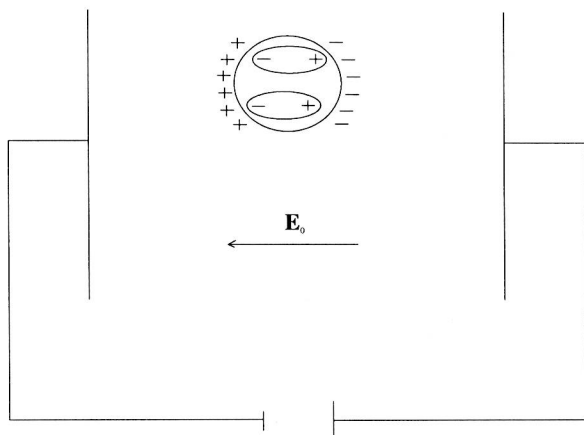
FIG. 1.1. The Lorentz cavity concept for definition of the local field $\mathbf{E}_{loc}$.

$$\mathbf{E}_{loc} = \mathbf{E}_0 + \mathbf{E}_d + \mathbf{E}_s + \mathbf{E}_{near}, \tag{1.1}$$

where $\mathbf{E}_0$ is the external field, $\mathbf{E}_d$ the depolarising field due to the bound charges on the outer surface of the dielectric medium, $\mathbf{E}_s$ the field due to bound charges on the surface S of the cavity, and $\mathbf{E}_{near}$ is due to the configuration of all nearby molecules. Now $\mathbf{E}_d$ is given by the charge density on the surface of the system, $\sigma_P = P_\perp = \pm P$, and hence

$$\mathbf{E}_d = -4\pi\mathbf{P}. \tag{1.2}$$

We can now connect the local field to the macroscopic field $\mathbf{E}$, since the normal component of the displacement $\mathbf{D}$ is continuous across the vacuum-dielectric boundary:

$$\mathbf{D} = \mathbf{E}_0 = \mathbf{E} + 4\pi\mathbf{P}. \tag{1.3}$$

Combining the above eqns (1.1)–(1.3) we have

$$\mathbf{E}_{loc} = \mathbf{E} + \mathbf{E}_s + \mathbf{E}_{near}. \tag{1.4}$$

This result is quite general and not specified only to the above geometry. The spherical polarisation field $\mathbf{E}_s$ is now easily evaluated using a continuum approximation, since the polarisation $\mathbf{P}$ can now be assumed to be uniform on the macroscopic scale. By elementary electrostatics (see, for example, Reitz and Milford 1970), then

$$\mathbf{E}_s = \mathbf{P} \int_0^{2\pi} \mathrm{d}\phi \int_0^\pi \mathrm{d}\theta \ \sin\theta \ \cos^2\theta = \frac{4\pi}{3}\mathbf{P}. \tag{1.5}$$

Now we come to the field $\mathbf{E}_{near}$ that is due to the dipoles inside S. There are a few cases for which this term vanishes, for instance in a gas or a liquid, where

these dipoles are distributed randomly in uncorrelated positions. This is also true for a cubic crystal, since

$$\mathbf{E}_{near} = \sum_{i,j,k} \frac{3\mathbf{p}.\mathbf{r}_{ijk}\mathbf{r}_{ijk} - \mathbf{r}_{ijk}^2\mathbf{p}}{\mathbf{r}_{ijk}^5}, \tag{1.6}$$

where $\mathbf{r}_{ijk}$ is the radius vector of a molecule on the lattice point (i, j, k). Scrutiny of the various terms shows that a typical component $\mathbf{E}_x$, say, has the form

$$\mathbf{E}_{near} = \sum_{i,j,k} \frac{.3(i^2 \ \mathbf{p}_x + ij \ \mathbf{p}_y + ik \ \mathbf{p}_z) - (i^2 + j^2 + k^2)\mathbf{p}_x}{a^3(i^2 + j^2 + k^2)^{\frac{5}{2}}}, \tag{1.7}$$

where a is the lattice spacing. Clearly, the cross-terms $(ij \ \mathbf{p}_y + ik \ \mathbf{p}_z)$ vanish, while the remaining terms cancel by cubic symmetry. This holds similarly for the other components $\mathbf{E}_y$ and $\mathbf{E}_z$ respectively. Finally, we can now write the local field $\mathbf{E}_{loc}$ as

$$\mathbf{E}_{loc} = \mathbf{E} + \frac{4\pi}{3}\mathbf{P}, \tag{1.8}$$

which is the famous Lorentz local field relation. The reader might note that sometimes, as will the case for the rest of this book, we may assume that the depolarising field $\mathbf{E}_d$ is known for a given sample. In any case it is dependent on a given sample surface geometry, which is a peripheral problem, as we are mainly interested in the properties of a bulk material. In this case we shall ignore $\mathbf{E}_d$ and define the local field to be

$$\mathbf{E}_{loc} = \mathbf{E}_0 + \frac{4\pi}{3}\mathbf{P}. \tag{1.9}$$

There remains the problem of the size of the Lorentz sphere. Obviously, this has to be of the order of the length scales for which Maxwell's equations are to be averaged, i.e. several lattice spacings or tens of Å. While there have been several criticisms of Lorentz's approach, including Landauer (1978), which caution the assumption of point dipole molecules in the above, the result given in eqn (1.9) is generally held to be true, as long as the polarisable entities are not too pathological; for example, for flat discs, see Cohen et al. (1973). Even for such cases, eqn (1.9) can of course be generalised by modifying $4\pi/3$ to $4\pi\sigma_{\alpha\beta}/3$, where $\sigma_{\alpha\beta}$ is an appropriate second rank tensor. However, difficulties remain in the case of inclusions whose shapes are not spherical, as we shall see later in deriving the Maxwell–Garnett formula in section 1.3.

Before moving on from here, we shall mention a few pitfalls of the Lorentz field concept, some of which will be discussed at length later. Here we should mention Rayleigh's attempts at finding exactly soluble models, like dipoles on a regular periodic lattice to evaluate the validity of Lorentz's concept. More recently, computer simulations have allowed more complex systems to be studied in this way. Even without these sophisticated studies, it is perhaps noteworthy

that the cavity concept must have its limitations. First, the cavity shape is in general ill-defined and it is unclear if it has significance in general. Secondly, the size of the cavity, if it coincides with the length scales of the averaging process must be involved in the very process which defines the macroscopic fields. Some form of self-consistency condition must therefore be required for a satisfactory theory. Finally, the identification of a particular molecule as the centre of the cavity leads to certain diffculties which culminate in the Lorentz catastrophe (see section 1.3), giving the concept a final blow.[3]

1.2   Clausius–Mossotti

The Clausius–Mossotti relation, perhaps one of the earliest formulae advanced, relates a macroscopic property (e.g. the dielectric constant ϵ) to a microscopic property (e.g. the molecular polarisability α). The relation has been used for instance by Einstein in 1910 (see, for example, Jackson 1975), in his treatment of the critical opalescence. This is the phenomenon of enhanced light scattering near the critical point of a fluid due to large density fluctuations. The derivation of the relation is straightforward and it rests solely on the Lorentz local field concept. Its proof consists of first identifying the connection between the dipole moment of the molecule with the local field E_{loc} via the molecular polarisability α. Thereafter the Lorentz field relation given in eqn (1.9) is invoked to derive the macroscopic polarisation $\mathbf{P}$ and hence the susceptibility χ in terms of α. Thus we start from the fact that the dipole moment of a molecule $\mathbf{p}$ is given by

$$\mathbf{p} = \alpha\,\mathbf{E}_{loc}, \tag{1.10}$$

where α is the polarisability. Then the polarisation $\mathbf{P}$ for the crystal is

$$\mathbf{P} = \sum_j N_j\mathbf{p}_j = \sum_j N_j\alpha_j\,\mathbf{E}_{loc}(j). \tag{1.11}$$

Here the sum is over all molecules j, whose polarisabilities are α_j with the local field $\mathbf{E}_{loc}(j)$ at that site, and N_j is the number of molecules per unit volume.[4] Assuming that the local field is identical for all sites, we can substitute eqn (1.8) for the local field $\mathbf{E}_{loc}$ in eqn (1.11), which leads to

$$\mathbf{P} = \left(\sum_j N_j\alpha_j\right)\left(\mathbf{E} + \frac{4\pi}{3}\mathbf{P}\right). \tag{1.12}$$

We obtain the dielectric susceptibility by solving for $\mathbf{P}$ as

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[3]Although the empirical successes in condensed matter physics attest to Minkowski's formulation of the macroscopic Maxwell equations (Jackson 1975, Kong 1990), this failure of Lorentz's scheme (see also the previous footnote) indicates that an adequate microscopic foundation for the macroscopic Maxwell's equations is still presently lacking.

[4]In a solid we should take α as a 'renormalised' polarisability, not necessarily identical with that of a single molecule in free space.