Muhammad Sahimi

Heterogeneous Materials I Linear Transport and Optical Properties

With 145 Illustrations



Muhammad Sahimi Department of Chemical Engineering University of Southern California Los Angeles, CA 90089-1211 USA and Institute for Advanced Studies in Basic Sciences Gava Zang, Zanjan 45195-159 Iran moe@iran.usc.edu

Editors S.S. Antman Department of Mathematics and Institute for Physical Science and Technology University of Maryland College Park, MD 20742 USA ssa@math.umd.edu

L. Sirovich Division of Applied Mathematics Brown University Providence, RI 02912 USA chico@camelot.mssm.edu J.E. Marsden Control and Dynamical Systems Mail Code 107-81 California Institute of Technology Pasadena, CA 91125 USA marsden@cds.caltech.edu

S. Wiggins School of Mathematics University of Bristol Bristol BS8 1TW UK s.wiggins@bris.ac.uk

Mathematics Subject Classification (2000): 82-02, 65M

Library of Congress Cataloging-in-Publication Data Sahimi, Muhammad. Heterogeneous materials / Muhammad Sahimi. p. cm. — (Interdisciplinary applied mathematics ; 22-23) Includes bibliographical references and indexes. Contents: [1] Linear transport and optical properties — [2] Nonlinear and breakdown properties and atomistic modeling. ISBN 0-387-00167-0 (v. 1 : alk. paper) — ISBN 0-387-00166-2 (v. 2 : alk. paper) 1. Inhomogeneous materials. 2. Composite materials. 1. Title. II. Interdisciplinary applied mathematiccs ; v. 22-23. TA418.9.153 S24 _ 2003 620.1'1—dc21 _ 2002042744

ISBN 0-387-00167-0 Printed on acid-free paper.

© 2003 Springer-Verlag New York, Inc.

All rights reserved. This work may not be translated or copied in whole or in part without the written permission of the publisher (Springer-Verlag New York, Inc., 175 Fifth Avenue, New York, NY 10010, USA), except for brief excerpts in connection with reviews or scholarly analysis. Use in connection with any form of information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed is forbidden. The use in this publication of trade names, trademarks, service marks, and similar terms, even if they are not identified as such, is not to be taken as an expression of opinion as to whether or not they are subject to proprietary rights.

Printed in the United States of America.

www.springer-ny.com

Springer-Verlag New York Berlin Heidelberg A member of BertelsmannSpringer Science+Business Media GmbH

CONTENTS

Preface

1. Introduction

- 1.0 Historical Perspective
- 1.1 Heterogeneous Materials
- 1.2 Effective Properties of Heterogeneous Materials
- 1.3 Linear Transport Properties
 - 1.3.1 The effective conductivity
 - 1.3.2 The effective dielectric constant
 - 1.3.3 The effective elastic moduli
- 1.4 Non-linear Transport Properties
 - 1.4.1 Constitutive non-linearity
 - 1.4.2 Threshold non-linearity
- 1.5 Predicting the Effective Properties of Heterogeneous Materials
 - 1.5.1 The continuum models
 - 1.5.2 The discrete models
- 1.6 The Organization of the Book

PART I:

CHARACTERIZATION AND MODELLING OF THE MORPHOLOGY

2. Characterization of Connectivity and Clustering

- 2.0 Introduction
- 2.1 Characterization of the Geometry: Self-Similar Fractal Microstructures
- 2.2 Statistical Self-Similarity
- 2.3 Measurement of the Fractal Dimension
 - 2.3.1 The correlation function method
 - 2.3.2 Small-angle scattering
- 2.4 Self-Affine Fractals
- 2.5 Characterization of Connectivity and Clustering

- 2.5.1 Random bond and site percolation
- 2.5.2 Percolation thresholds
- 2.5.3 Bicontinuous materials, phase-inversion symmetry, and percolation
- 2.5.3 Computer generation of a single cluster
- 2.6 Percolation Properties
 - 2.6.1 Morphological properties
 - 2.6.2 Transport properties
 - 2.6.3 The structure of the sample-spanning cluster
- 2.7 Universal Scaling Properties of Percolation
 - 2.7.1 Morphological properties
 - 2.7.2 Transport properties
 - 2.7.3 Practical significance of the critical exponents
- 2.8 Scale-Dependent Properties of Percolation Composites
- 2.9 Finite-Size Scaling
- 2.10 Percolation in Random Networks and Continua
 - 2.10.1 Percolation thresholds: Materials with very low or high thresholds
 - 2.10.2 The Ornstein-Zernike formulation
- 2.11 Differences between Lattice and Continuum Percolation
- 2.12 Correlated Percolation
 - 2.12.1 Short-range correlations
 - 2.12.2 Long-range correlations
- 2.13 Experimental Measurement of Percolation Properties

Summary

3. Characterization and Modelling of the Morphology

- 3.0 Introduction
- 3.1 Models of Heterogeneous Materials
- 3.2 One-Dimensional Models
- 3.3 Spatially-Periodic Models
- 3.4 Continuum Models
 - 3.4.1 Dispersion of spheres

3.4.1.1 Equilibrium hard-sphere model

3.4.1.2 Random close packing versus maximally random jamming

3.4.1.3 Particle distribution and correlation functions

3.4.1.4 The n-particle probability density

3.4.2 Distribution of equal-size particles

3.4.2.1 Fully-penetrable spheres

3.4.2.2 Fully-impenetrable spheres

3.4.2.3 Interpenetrable spheres

3.4.3 Distribution of polydispersed spheres

3.4.3.1 Fully-penetrable spheres

3.4.3.2 Fully-impenetrable spheres

3.4.4 Simulation of dispersion of spheres

3.4.5 Models of anisotropic materials

3.4.6 Tessellation models of cellular materials

3.4.7 Gaussian random field models of amorphous materials

3.5 Discrete Models

3.5.1 Network models

3.5.2 Bethe lattice models

3.6 Reconstruction of Heterogeneous Materials: Simulated Annealing

Summary

PART II:

LINEAR TRANSPORT AND OPTICAL PROPERTIES

4. Effective Conductivity, Dielectric Constant and Optical Properties: The Continuum Approach

4.0 Introduction

4.1 Symmetry Properties of the Conductivity Tensor

4.2 General Results

4.3 Effective Conductivity of Dispersion of Spheres: Exact Results

4.3.1 Three-dimensional regular arrays of spheres

4.3.1.1 Simple-cubic arrays

4.3.1.2 Body-centered and face-centered cubic arrays

4.3.2 Two-dimensional arrays of cylinders

4.3.2.1 Hexagonal arrays

4.3.2.2 Square arrays

- 4.4 Exact Results for Coated Spheres and Laminates
- 4.5 Perturbation Expansion for the Effective Conductivity
 - 4.5.1 Isotropic materials: Strong contrast expansion
 - 4.5.2 Approximations
 - 4.5.3 The microstructural parameter ζ_2
 - 4.5.4 Anisotropic materials
- 4.6 Bounds to the Effective Conductivity
 - 4.6.1 Isotropic materials
 - 4.6.1.1 Two-point bounds
 - 4.6.1.2 Cluster bounds
 - 4.6.1.3 Three- and four-point bounds
 - 4.6.1.4 Cluster expansions for the effective conductivity
 - 4.6.2 Anisotropic materials
 - 4.6.2.1 Two-point bounds
 - 4.6.2.2 Three- and four-point bounds
 - 4.6.2.3 Simplification of the bounds
 - 4.6.2.4 Cluster expansions for the effective conductivity
- 4.7 The Effect of the Interface on the Effective conductivity
- 4.8 Exact Duality Relations
- 4.9 Effective-Medium Approximation
 - 4.9.1 Isotropic materials
 - 4.9.2 Anisotropic materials
 - 4.9.3 Critique of the effective-medium approximation
 - 4.9.4 The Maxwell-Garnett approximation
- 4.10 The Random Walk Method
- 4.11 The Effective Dielectric Constant
 - 4.11.1 Spectral representation

- 4.11.2 Perturbation expansion
- 4.11.3 Rigorous bounds
- 4.12 Optical Properties
 - 4.12.1 Conductor-insulator composites
 - 4.12.2 Conductor-superconductor composites
 - 4.12.3 Anisotropic materials
 - 4.12.4 The Cole-Cole representation
- 4.13 Beyond Quasi-Static Approximation: Mie Scattering
- 4.14 Dynamical Effective-Medium Approximation
- 4.15 The Effect of Large-Scale Morphology
- 4.16 Multiple-Scattering Approach

Summary

5. Effective Conductivity and Dielectric Constant: The Discrete Approach

- 5.0 Introduction
- 5.1 Experimental Data for Conduction in Heterogeneous Materials
 - 5.1.1 Powders
 - 5.1.2 Polymer composites
 - 5.1.3 Conductor-insulator composites
- 5.2 Conductivity of a Random Resistor Network
- 5.3 Exact Solution for the Bethe Lattices
 - 5.3.1 The microscopic conductivity
 - 5.3.2 Effective-medium approximation
 - 5.3.3 Conductor-insulator composites
 - 5.3.4 Conductor-superconductor composites
- 5.4 Exact Results for Two-Dimensional Composites
 - 5.4.1 Exact duality relations
 - 5.4.2 Log-normal conductance distribution
- $5.5\ {\rm Green}\ {\rm Function}\ {\rm Formulation}\ {\rm and}\ {\rm Perturbation}\ {\rm Expansion}$
 - 5.5.1 Properties of the Green Functions
- 5.6 Effective-medium approximation

- 5.6.1 Conductor-insulator composites
- 5.6.2 Conductor-superconductor composites
- 5.6.3 Resistor networks with multiple coordination numbers
- 5.6.4 Materials with zero percolation threshold
- 5.6.5 Comparison with the experimental data
- 5.6.6 Accuracy of the effective-medium approximation
- 5.6.7 Cluster effective-medium approximation
- 5.6.8 Coherent-potential approximation
- 5.7 Effective-Medium Approximation for Site Percolation
- 5.8 Effective-Medium Approximation for Correlated Composites
- 5.9 Effective-Medium Approximation for Anisotropic Materials
 - 5.9.1 The Green functions
 - 5.9.2 Conductivity anisotropy near the percolation threshold
 - 5.9.3 Comparison with the experimental data
- 5.10 Cumulant Approximation
 - 5.10.1 The Lorentz field
 - 5.10.2 Perturbation expansion
 - 5.10.3 Computation of the lowest-order terms
 - 5.10.4 Bond percolation
- 5.11 Position-Space Renormalization Group Methods
- 5.12 Renormalized Effective-Medium Approximation
- 5.13 The Critical Path Method
- 5.14 Numerical Computation of the Effective Conductivity
 - 5.14.1 The conjugate-gradient method
 - 5.14.2 Transfer-matrix method
 - 5.14.3 Network reduction: The Lobb-Frank-Fogelholm methods
 - 5.14.4 Random walk method
- 5.15 Estimation of the Critical Exponent of Conductivity
 - 5.15.1 Finite-size scaling
 - 5.15.2 Position-space renormalization group method
 - 5.15.3 Series expansion

5.15.4 Field-theoretic approach

- 5.15.5 Comparison with the experimental data
- 5.16 Resistance Fluctuations, Moments of the Current Distribution, and Flicker Noise
 - 5.16.1 Tellegen's theorems
 - 5.16.2 Cohn's theorems
 - 5.16.3 Scaling properties
 - 5.16.4 Comparison with the experimental data

5.17 Hall Conductivity

- 5.17.1 Effective-medium approximation
- 5.17.2 Network model
- 5.17.3 Exact duality relations
- 5.17.4 Scaling properties
- 5.17.5 Comparison with the experimental data
- 5.18 Classical Aspects of Superconductivity
 - 5.18.1 Magnetoconductivity
 - 5.18.2 Magnetic properties
 - 5.18.3 Comparison with the experimental data
 - 5.18.3.1 The London penetration depth
 - 5.18.3.2 The specific heat
 - 5.18.3.3 The critical current
 - 5.18.3.4 The critical fields
 - 5.18.3.5 Differential diamagnetic susceptibility

Summary

6. Frequency-Dependent Properties: The Discrete Approch

- 6.0 Introduction
- 6.1 Diffusion in Heterogeneous Materials
 - 6.1.1 Green function formulation and perturbation expansion
 - 6.1.2 Self-consistent approach
 - 6.1.3 Self-consistent, generalized master equation, and continuous-time random walks
 - 6.1.4 The Green functions

- 6.1.5 Effective-medium approximation
- 6.1.6 The mean square displacement
- 6.1.7 Difference between transport in low- and high-dimensional materials
- 6.1.8 Predictions of the effective-medium approximation

6.1.8.1 One-dimensional materials

6.1.8.2 Two- and three-dimensional materials

6.1.9 Anomalous diffusion

6.1.10 Scaling theory of anomalous diffusion

6.1.11 Comparison with the experimental data

6.1.12 The governing equation for anomalous equation

6.2 Hopping Conductivity

- 6.2.1 The Miller-Abraham network model
- 6.2.2 The symmetric hopping model

6.2.2.1 Exact solution for one-dimensional materials

6.2.2.2 Exact solution for Bethe lattices

- 6.2.2.3 Perturbation expansion and effective-medium approximation
- 6.2.3 The asymmetric hopping model: Perturbation expansion
 - 6.2.3.1 Exact solution for Bethe lattices
 - 6.2.3.2 Two-site self-consistent approximation
 - 6.2.3.3 Two-site effective-medium approximation
 - 6.2.3.4 Energy-dependent effective-medium approximation
- 6.2.4 Variable-range hopping: The critical path method

6.2.4.1 Effect of a variable density of states

6.2.4.2 Effect of Coulomb interactions

6.2.4.3 Comparison with the experimental data

6.2.4.4 Fractal morphology and superlocalization

6.2.5 Continuous-time random walk model

6.3 AC Conductivity

6.3.1 Universality of AC conductivity

- 6.3.2 Resistor-capacitor model
- 6.3.3 Universal AC conductivity: Effective-medium approximation

- 6.3.4 Universal AC conductivity: Symmetric hopping model
- 6.3.5 Role of percolation in universality of AC conductivity
- 6.4 Dielectric Constant and Optical Properties
 - 6.4.1 Resistor-capacitor model
 - 6.4.2 Resistor-capacitor-inductor model
 - 6.4.3 Position-space renormalization group approach
 - 6.4.4 Effective-medium approximation
 - 6.4.5 Random walk model
- 6.5 Scaling Properties of AC Conductivity and Dielectric Constant
 - 6.5.1 Comparison with the experimental data
- 6.6 Vibrational DEnsity of States: The Scalar Approximation
 - 6.6.1 Numerical computations
 - 6.6.2 Effective-medium approximation
 - 6.6.3 Cluster effective-medium approximation
 - 6.6.4 Scaling theory: Phonons versus fractons
 - 6.6.5 Characteristics of fractons
 - 6.6.5.1 Localization
 - 6.6.5.2 Dispersion relation
 - 6.6.5.3 Crossover from phonons to fractons
 - 6.6.6 Large-scale computer simulations
 - 6.6.7 Missing modes
 - 6.6.8 Localization properties of fractons
 - 6.6.8.1 Modes patterns of fractons
 - 6.6.8.2 Ensemble-averaged fractons
 - 6.6.9 Comparison with the experimental data
- 6.7 The Dynamical Structure Factor
 - 6.7.1 Theoretical analysis
 - 6.7.2 Scaling analysis
 - 6.7.3 Numerical computation

6.8 Fractons and Thermal Transport in Inhomogeneous Materials

6.8.1 Anharmonicity

6.8.2 Phonon-assisted fracton hopping

6.8.3 Dependence of sound velocity on temperature

Summary

7. Rigidity and Elastic Properties: The Continuum Approach

7.0 Introduction

- 7.1 The Stress and Strain Tensors
 - 7.1.1 Symmetry Properties of the stiffness tensor
 - 7.1.2 Theorems of minimum energy
 - 7.1.3 The strain energy of a composite material
 - 7.1.4 Volume averaging

7.2 Exact Results

- 7.2.1 Interrelations between two- and three-dimensional moduli
- 7.2.2 Exact results for regular arrays of spheres
- 7.2.3 Exact results for coated spheres and laminates
- 7.2.4 Connection to two-dimensional conductivity
- 7.2.5 Exact duality relations
- 7.2.6 The Cherkaev-Lurie-Milton theorem and transformation
- 7.2.7 Universality of Poisson's ratio in percolation composites
- 7.2.8 Composite materials with equal shear moduli
- 7.2.9 Dundurs constants
- 7.2.10 Relation between elastic moduli and thermoelastic properties
- 7.3 Dispersion of Spherical Inclusions
 - 7.3.1 The dilute limit: A single sphere
 - 7.3.2 Non-dilute systems
 - 7.3.3 Two spherical inclusions
- 7.4 Exact Strong-Contrast Expansions
 - 7.4.1 Integral equation for the cavity strain field
 - 7.4.2 Exact series expansions
 - 7.4.3 Exact series expansions for isotropic materials
 - 7.4.4 Macroscopically-anisotropic materials

7.4.5 The microstructural parameter η_2

7.4.6 Comparison with numerical simulation

7.4.6.1 Two-dimensional materials

7.4.6.2 Three-dimensional materials

7.5 Rigorous Bounds

7.5.1 Isotropic materials

7.5.1.1 One-point bounds

7.5.1.2 Two-point bounds

7.5.1.3 Cluster bounds

7.5.1.4 Three- and four-point bounds

7.5.2 Anisotropic materials

7.6 Multiple Scattering Method

7.6.1 The dilute limit

7.6.2 Non-dilute systems

7.6.3 Comparison with the experimental data

7.7 Effective-Medium Approximation

7.7.1 Fundamental tensors and invariant propertries

7.7.2 Symmetric effective-medium approximation

7.7.3 Asymmetric effective-medium approximation

7.7.4 The Maxwell-Garnett approximations

7.8 Numerical Simulation

7.8.1 Finite-difference methods

7.8.2 Boundary-element and finite-element methods

7.9 Links between the Conductivity and Elastic Moduli

7.9.1 Two-dimensional materials

7.9.1.1 Conductivity-bulk modulus bounds

7.9.1.2 Conductivity-shear modulus bounds

7.9.1.3 Applications

7.9.2 Three-dimensional materials

7.9.2.1 Conductivity-bulk modulus bounds

7.9.2.2 Applications

Summary

8. Rigidity and Elastic Properties: The Discrete Approach

- 8.0 Introduction
- 8.1 Elastic Networks in Biological Materials
- 8.2 Number of Elastic Moduli of a Lattice
- 8.3 Numerical Simulation and Finite-Size Scaling
- 8.4 Derivation of Elastic Networks from Continuum Elasticity
 - 8.4.1 The Born model
 - 8.4.2 Shortcomings of the Born model
- 8.5 The Central-Force Network
- 8.6 Rigidity Percolation
 - 8.6.1 Static and dynamic rigidity and floppiness of networks
 - 8.6.2 The correlation length of rigidity percolation
 - 8.6.3 The force distribution
 - 8.6.4 Determination of the percolation threshold
 - 8.6.4.1 Moments of the force distribution
 - 8.6.4.2 The pebble game
 - 8.6.4.3 Constraint-counting method
 - 8.6.5 Mapping between rigidity percolation and resistor networks
 - 8.6.6 Nature of phase transition in rigidity percolation
 - 8.6.7 Scaling properties of the elastic moduli
- 8.7 Green Function Formulation and Perturbation Expansion
 - 8.7.1 Effective-medium approximation
 - 8.7.2 The Born model
 - 8.7.3 Rigidity percolation
- 8.8 The Critical Path Method
- 8.9 Central-Force Networks at Non-zero Temperature and under Stress
- 8.10 Shortcomings of the Central-Force Networks
- 8.11 Elastic Percolation Networks with Bond-Bending Forces
 - 8.11.1 The Kirkwood-Keating model

- 8.11.2 The bond-bending model
- 8.11.3 The percolation thresholds
- 8.11.4 The force distribution
- 8.11.5 Comparison of the central-force and bond-bending networks
- 8.11.6 Scaling properties
- 8.11.7 Relation with scalar percolation
- 8.11.8 Fixed points of vector percolation: Universality of the Poisson's ratio
- 8.11.9 Position-space renormalization group method
- 8.11.10 Effective-medium approximation
- 8.12 Transfer-Matrix Method
- 8.13 The Beam Model
- 8.14 The Granular Model
- 8.15 Entropic Networks
- Summary

9. Rigidity and Elastic Properties of Network Glasses, Polymers, and Composite Solids:

The Discrete Approach

- 9.0 Introduction
- 9.1 Network Glasses
 - 9.1.1 Rigidity transition
 - 9.1.2 Comparison with the experimental data
 - 9.1.3 Rigidity transition at high coordination numbers
 - 9.1.4 Effect of one fold-coordinated atoms
 - 9.1.5 Stress-free versus stressed transition
- 9.2 Branched Polymers and Gels
 - 9.2.1 Percolation model of polymerization and gelation
 - 9.2.2 Morphological properties of branched polymers and gels
 - 9.2.2.1 Gel polymers
 - 9.2.2.2 Comparison with the experimental data
 - 9.2.2.3 Branched polymers

9.2.2.4 Comparison with the experimental data

- 9.2.3 Rheology of critical gels: Dynamic-mechanical experiments
- 9.2.4 The relaxation time spectrum
- 9.2.5 Comparison with the experimental data
 - 9.2.5.1 Physical gels
 - 9.2.5.2 Chemical gels
 - 9.2.5.3 Enthalpic versus entropic elasticity
 - 9.2.5.4 Viscosity of near critical gelling solutions
- 9.3 Mechanical Properties of Foams
- 9.4 Mechanical Properties of Composite Solids
 - 9.4.1 Porous materials
 - 9.4.2 Superrigid materials
- 9.5 Wave speeds in Porous Materials
- 9.6 Elastic Properties of Composite Materials with Length Mismatch
- 9.7 Materials with Negative Poisson's Ratio
- 9.8 Vibrational Density of States: Vector Percolation Model
 - 9.8.1 Scaling theory
 - 9.8.2 Crossover between scalar approximation and vector density of states
 - 9.8.3 Large-scale computer simulation
 - 9.8.4 Comparison with the experimental data

Summary

References

Index