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Transport Processes in Macroscopically Disordered Media

From Mean Field Theory to Percolation

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Dedicated to the memory of A.M. Dykhne

Preface

The basic problem described in this book is how one can find effective characteristics such as conductivity, dielectric permittivity, magnetic permeability, etc., knowing the distribution of different components constituting inhomogeneous medium.

We consider here a wide range of recent studies dedicated to the elucidation of the physical properties of macroscopically disordered systems. They are galvano-electric, thermoelectric, and elastic properties as well as behavior of 1/*f*-noise, current moments, and higher harmonic generation in composites at the threshold of percolation. Our goal in writing this book is to reflect on recent advances in our understanding of percolation systems and to present in coherent fashion a very wide range of transport phenomena in inhomogeneous disordered systems. We also tried to use, as much as possible, unifying treatment that would allow interdisciplinary view of apparently diverse physical properties to be treated at equal footing. We also regret in retrospect that many important areas of recent activities in field have not been included such as thermoelectric properties of composites.

The unity of treatments, by authors deep conviction, is main thrust here: connects phenomena that seem to be very different and yet so close under closer investigation. Their appearance seems to be strange under one book. For instance, one would not expect to see 1/f noise in percolation systems together with pinning and Abrikosov vortexes. Authors were trying to present material in a way to make it readily available to a typical reader who is familiar with undergraduate physics courses and is trying to familiarize himself with active research avenues in the advanced fields of condensed matter sciences, materials, etc. It is our hope that that present book would enable serious advance student to obtain most of described results with minimum time and paper. We use hierarchical model and believe that it is the most straightforward way to arrive at basic physical properties of complicated systems along with corresponding qualitative characteristics and functional dependencies.

We did not try to write a classic exhausting monograph, but rather straightforward set of useful tools and even recipes, so that reader could almost immediately "see" and "try" and even "feel" by his own hands or with simplest MathCad what and how composites behave.

Material of this book is presented in three parts. In the first one we describe two classes of the methods of studying macroscopically disordered media. In this first class we include mainly mean field techniques, which typically give reliable results in the cases when density number of one of phases is much smaller compared with another. Sometimes they work even for large density.

The second class of methods is usually intended to describe processes in vicinity of the threshold of percolation when small changes in number densities may cause big changes. One of the models is the so-called hierarchical model. In the second part of this book we consider the application of different techniques to a broad spectrum of physical properties of composites roughly one per chapter. The reader has to realize that it is next to impossible to study but all phenomena of transport in composites. Most obvious omissions are mechanical and electrical disruption of materials such as composites, processes of fluid dynamics in porous media, thermogalvanomagnetic phenomena, conductivity of many component media, quantum Hall effect, etc. Decisive role in our interest to what is described in this book was initiated by A.M. Dykhne. We dedicate this book to him.

We want to express our gratitude to many of our friends and coworkers. Many topics that have been exposed here benefited heavily on them. We thank I. Adrianov, B. Aranson, V. Archincheev, E. Baskin, E. Belozky, D. Bergman, J.L. Birman, A. Dzedzits, I. Kaganova, V. Kholod, A. Kolek, S. Kucherov, A. Lagarkov, B. Lev, B. Linchersky, S. Lukyanets, A. Palti, E. Pashitsky, A. Sarychev, A. Satanin, M. Shamonin, L. Shepp, A. Shik, B. Shklovskii, K. Slipchenko, Y. Strelniker, P. Tomchuk, K. Usenko, A. Vinogradov, and M. Zhenirovsky. We also thank CUNY for assistance.

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References

1. Antonov AC et al. (ed. Lagar'kov AN) (1990) Electrophysical properties of percolation systems. Moscow, IBTAN, 120 pp (in Russian)
2. Beran AM (1974) Application of statistical theories for the determination of thermal, electrical, and magnetic properties of heterogeneous materials. In: Sendeckyj GP (ed) Mechanics of composite materials, vol 2. Academic Press, San Diego, CA, p. 209–249
3. Berdichevsky V (2009) Variational principles of continuous mechanics I. Fundamentals. Springer, 529 pp

4. Berdichevsky V (2009) Variational principles of continuous mechanics II. Applications. Springer, 430pp
5. Bergman DJ, Stroud D (1992) Physical properties of macroscopically inhomogeneous media. Solid State Phys 46, 147–269
6. Clerc JP, Giraud G, Laugier JM and et al. (1990) The electrical conductivity of binary disordered systems, percolation clusters, fractals and related models. Adv Phys 39, 191–309
7. Cohen R, Havlin S (2010) Complex networks structure, robustness and function, 248pp
8. Ewing R, Hunt A (2009) Percolation theory for flow in porous media. In: Lecture notes in physics, 771pp
9. Hunt A, Ewing R, Ghanbarian B (2014) Percolation theory for flow in porous media 3rd ed., Springer, 446pp
10. Isichenko MB (1992) Percolation, statistical topography, and transport in random media. Rev Mod Phys 64, 961–1043
11. Kirpatrick S (1973) Percolation and conduction. Rev Mod Phys 45, 574–588
12. Nakayama T, Yakubo K, Orbach RL (1994) Dynamical properties of fractal networks: scaling, numerical simulation, and physical realization. Rev Mod Phys 66, 381–443
13. Pobedrja BE (1984) Mechanics of composite materials. Moscow University, 336pp (in Russian)
14. Sahimi M (1993) Flow phenomena in rocks: from continuum models to fractals, percolation, cellular automata, and simulated annealing. Rev Mod Phys 65, 1393–1534
15. Sahimi M (1994) Applications of percolation theory. Taylor&Francis, 258pp
16. Sahimi M (1998) Non-linear and non-local transport processes in heterogeneous media: from long-range correlated percolation to fracture and materials breakdown. Phys Rep 306, 213–395
17. Shvidler M (1985) Statistical hydromechanics of porous media. Nedra, Moscow, 288pp (in Russian)
18. Stauffer D, Aharony A (1992) Introduction to percolation theory, 2nd edn. Taylor&Francis, 181pp
19. Tarasevich Y (2002) Percolation: theory, applications and algorithms URSS. Moscow, 112pp. (in Russian)
20. Torquato S (2002) Random heterogeneous materials: microstructure and macroscopic properties, Springer-Verlag New York, 703pp
21. Vinogradov AP (2001) Electrodynamics of composite materials URSS. Moscow, 208pp. (in Russian)
22. Ziman JM (1979) Models of disorder: the theoretical physics of homogeneously disordered systems. Cambridge University Press, London, 538pp

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Part I
Methods

Chapter 1
Introduction

1.1 Types of Macroscopically Disordered Media

When we consider macroscopically inhomogeneous media we usually understand that the characteristic sizes of inhomogeneity is much greater compared with any characteristic macroscopic lengths. For instance, if we consider DC conduction of the electric current, and we usually assume that we have a situation where the size of inhomogeneity is much larger than mean free path of the current density. In particular, this fact signifies that local Ohm's law is satisfied; connecting the current density $\mathbf{j}(\mathbf{r})$ to the electric field $\mathbf{E}(\mathbf{r})$ at arbitrary point of the medium $\mathbf{j}(\mathbf{r}) = \sigma(\mathbf{r})\mathbf{E}(\mathbf{r})$, and the nonuniformity of the medium is signaled by the special local conductivity $\sigma(\mathbf{r})$.

The macroscopic inhomogeneity may be continuous as well as discrete, depending on whether local conductivity $\sigma(\mathbf{r})$ is continuous or not. In the latter case we usually imply that we deal with two, three, and greater number of phases of media, where under word phase we understand set of regions with the common partial conductivities—$\sigma_1, \sigma_2, \ldots$.

There exist a huge number of different models of two-phased systems. For example, in some models it is assumed that there is set of spherical inclusions in host matrix. In more sophisticated models spherical shape is replaced by others shapes, ellipsoidal, for instance. In these cases one may introduce the distribution of the axial sizes of these ellipsoids, different characteristics of sizes of inclusions, different conductivities, etc. (see Fig. 1.1).

Effective kinetic coefficients correspond to the basic properties of transport processes in macroscopically disordered systems. They provide a global characterization of the inhomogeneous medium and describe basic physics due to typical sizes much larger compared to sizes of inhomogeneity of macroscopic deviations. In fact there are two fundamentally different treatments: in the former we assume the knowledge of local kinetic coefficients and we call it deterministic, in the latter

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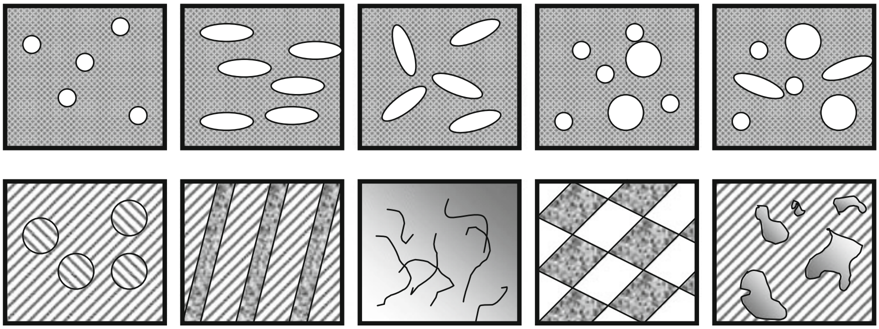

Fig. 1.1 Schematic representation of different disordered media: *Upper row*–one phase inclusions (*white area*) into the matrix; *lower row*—three pictures on the *left* show possible anisotropic inclusions

we know only them as random fields and we call it statistical one. Each of these treatments possesses their advantages and disadvantages. The deterministic treatment is usually applied for media with relatively simple structure; in the case of stochastic one we may experience definite difficulties with correlation between statistical description and physical observation of randomized disordered behavior of the kinetic coefficients. When one is trying to rigorously apply stochastic description he has to split original problem into two; first, estimation of kinetic coefficients at fixed dependence of local kinetic coefficients and only later should average over different realizations (ensembles). Effective kinetic coefficients, estimated at the first stage, always depend on concrete realization of local kinetic coefficients, though "… we always expect in correctly formulated theory the appearance of some kind of self-averaging, but, on the other hand, the theory as well as experiment deal with a sample of a certain realization" [3].

In what follows, we will always consider the self-averaging effective kinetic coefficients such as functionals of local kinetic coefficients, so that when sending the value of the volume of averaging to positive infinity, they approach the non-random limiting values. The process of self-averaging quantities has been extensively investigated in the quantum theory of random systems (see Chap. 2). There exists a very deep analogy between self-averaging in the quantum theory of random systems and the problems of foundations of classical statistical mechanics [2]. In fact one can see a very illuminating table in [1], where this analogy is traced rather directly. Following this example, we can supplement this idea with yet another Table (1.1) with data of local transport coefficients. Averages over volume of the field and the self-averaged currents do coincide with subsequent averages over all the realizations of random fields of local kinetic coefficients. Proceeding this way, one eventually needs only one concrete realization to determine effective unique set of kinetic coefficients.

Table 1.1 Correspondence between physical theories

Statistical mechanics	Theory of random systems	Macroscopically disordered medium
Phase space—space of points $\{p, q\}$, where p и q—sets of moments and coordinates	Space of functions $U(\mathbf{r})$, where $U(\mathbf{r})$—random potential, where carriers move	Space of functions like local kinetic coefficients, for instance local kinetic coefficients, such as local conductivity $\sigma(\mathbf{r})$
Any non-averaged physical function $f(p, q)$	Any non-averaged physical functional $A = A[U(\mathbf{r})]$	Fluxes and fields, for example $\mathbf{j} = \mathbf{j}[\sigma(\mathbf{r})]$ и $\mathbf{E} = \mathbf{E}[\sigma(\mathbf{r})]$
Time average corresponds to physical characteristics	Volume average corresponds to physical characteristics	Volume average corresponds to physical characteristics
Ergodic hypothesis: time average coincides with ensemble average	Ergodic hypothesis: average over volume coincides with mean over all random field realizations	Averaged fluxes and fields coincide with mean realizations of random fields of local kinetics

1.2 Classification of Physical Properties. Physical Analogies

Seemingly, a great number of different geometries signify the main difficulty in our ability of evaluation of the effective kinetic coefficients as functions of concentrations and their distribution. One unifying picture has never emerged. Situation is rather delicate and even there is not a simple answer to whether effective properties have to be anisotropic or not. We have to mention that no one ever suggested exhaustive complete classification of possible geometric phases. However, for each individual case such a description does exist; for example, two-phase systems with spherically shaped inclusions with known distribution function of different diameters. Of course, there exist much more sophisticated models of more complicated structures, for instance, those ones which include the information about macro- and micro-imperfections while their characteristic sizes could be bigger, equal, or smaller than mean free path and even more complicated ones.

Up to this point, we have mainly mentioned as an example of effective kinetic coefficients only effective electric conductivity, i.e., only for electric conduction in random media. However, many other kinetic processes, such as heat conduction, for instance, up to notational difference are very similar in their nature and could be treated accordingly (Table 1.2). Of course, we can mention problems of very different physical phenomena such as evaluation of elastic properties of random media, where a very different treatment is required.

Table 1.2 Different physical phenomena

Physical phenomena	Thermodynamic flux and equation, which describes it in stationary	Thermodynamic force and equation which describes it in stationary case	Law of physics
Electrical conductivity	$\mathbf{j}, \quad \operatorname{div} \mathbf{j} = 0$	$\mathbf{E}, \quad \operatorname{curl} \mathbf{E} = 0$	Ohm's law $\mathbf{j} = \sigma \mathbf{E}$
Thermal conductivity	$\mathbf{q}, \quad \operatorname{div} \mathbf{q} = 0$	$\mathbf{g} = -\nabla T, \quad \operatorname{curl} \mathbf{g} = 0$	Fourier's law $\mathbf{q} = \kappa \mathbf{g}$
Diffusion	$\mathbf{p}, \quad \operatorname{div} \mathbf{p} = 0$	$\mathbf{s} = -\nabla T, \quad \operatorname{curl} \mathbf{s} = 0$	Fick's law $\mathbf{p} = \kappa \mathbf{s}$

$\mathbf{j}$—electric current density, $\mathbf{E}$—electric field, $\mathbf{q}$—density of heat flow, $\mathbf{g} = -\nabla T$—temperature gradient, $\mathbf{p}$—density of flux of particles, $\mathbf{s} = -\nabla n$—gradient of number density

It is a rather surprising fact that there exists a whole family of problems of finding effective properties of the media with the macroscopic disorder which can be effectively reduced to above-mentioned technique. For Instance, the problem of high-temperature hopping conductivity in doped semiconductor is such a problem (Chap. 8).

References

1. Bonch-Bruevich V, Zvagin I, Kiper R et al (1981) Electronic theory of inhomogeneous semiconductors. Nauka, p 384 (in Russian)
2. Lifshits IM, Gredeskul SA, Pastur LA (1988) Introduction to the theory of disordered systems. Wiley, New York, p 462
3. Volovik GE, Dzyaloshinskiĭ IE (1978) Additional localized degrees of freedom in spin glasses. Sov Phys JETP 48:555–559

Chapter 2
The Methods of Description of Random Media

2.1 Effective Kinetic Coefficients, or What Do We Measure

In order to make an illustration of the description of a macroscopically random medium let us consider a sample, consistent mainly of some homogeneous material, which includes also one or two inclusions of another material and having simple geometric shape. One can solve the problem of spatial distribution, for example, of electric field in this sample exactly. If we consider sufficiently large number of inclusions and/or if they are randomly distributed, then we find that problem usually cannot be solved analytically and even numerically. Though, in many cases we do not even need to look for exact solution. In fact, we often are not even interested in detailed solution simply because typically in experiment we can measure only some averaged characteristics, such number densities of inclusions, their shapes, geometries, and sizes.

There exist media, for which, in many practical cases, one can obtain sufficient description. They are so-called uniform in mean. If one looks at sufficiently large samples of this medium, he finds their properties to be close to each other (Fig. 2.1).

Let us clarify the meaning of uniform in mean medium by the example of electrical conductivity in inhomogeneous electric conducting media. Suppose a local Ohm's law is valid, and thus $\mathbf{E}(\mathbf{r}) = \rho(\mathbf{r}) \cdot \mathbf{j}(\mathbf{r})$, where $\mathbf{E}(\mathbf{r})$—electric field, $\mathbf{j}(\mathbf{r})$—current density, and $\rho(\mathbf{r})$—local resistivity. Resistances of above mentioned pieces will be same even though their special orientations in each sample will be different. Figure 2.2 depicts measurement of resistance in such sample.

This resistance is a functional on $\mathbf{j}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$:

$$R = R[\mathbf{j}(\mathbf{r}), \mathbf{E}(\mathbf{r})]. \tag{2.1.1}$$

Let us pick an electric resistivity which we will call as ρ_{e}, such that the total resistance of the same shape and size of homogeneous conductor R_{e} would be equal R, Fig. 2.3. This medium might be called medium of comparison.

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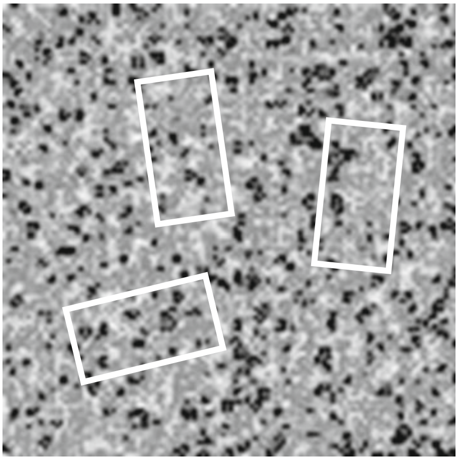


Fig. 2.1 Microscopically inhomogeneous medium. Shown are microscopically different samples of medium, with the same characteristics

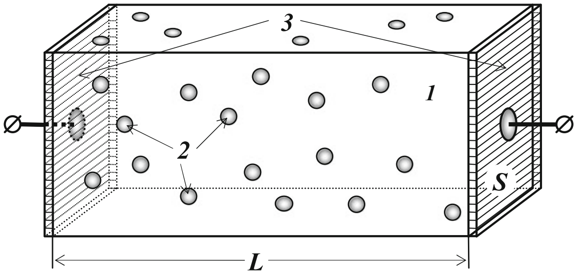


Fig. 2.2 Measuring resistance of the sample of the uniform in mean. *1*, *2*—phases making up the medium, *3*—pieces of contact ($\rho_3 \ll \rho_{1,2}$)

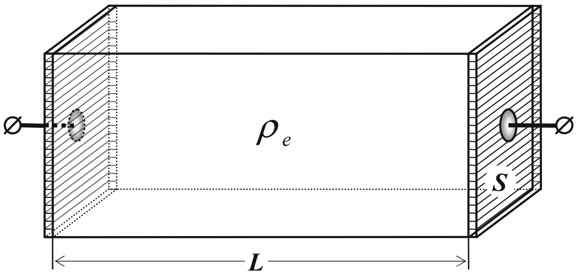


Fig. 2.3 A sample of the medium of comparison, which coincides with the similar sample of the chosen inhomogeneous media

Simple analysis shows, that ρ_e—coefficient of proportionality between $\langle \mathbf{E} \rangle$ and average current density

$$\langle \mathbf{E} \rangle = \rho_e \langle \mathbf{j} \rangle, \tag{2.1.2}$$

Indeed, for the sample of the length L and cross-sectional area S while $\langle \mathbf{E} \rangle \parallel \langle \mathbf{j} \rangle$ one can write (we skip here obvious vector notation)

$$\langle E\rangle L = \rho_e L(\langle j\rangle S/S),$$

Thus voltage $U = \langle E\rangle L$ and current $I = \langle j\rangle S$ are related through following formula

$$U = (\rho_e L/S)I,$$

In the other words, we obtain the well-known relationship for a resistance of a sample, measured in typical experiment

$$R_e = \rho_e L/S, \qquad (2.1.3)$$

We give here the definition of macroscopically inhomogeneous medium. It is a medium where the characteristic size of inhomogeneity a_0 is much larger than any typical physical characteristics ℓ, for instance, mean-free-path of electric charge. We express this fact by writing the following inequalities

$$\sqrt[3]{V} \gg a_o \gg \ell, \qquad (2.1.4)$$

where $\sqrt[3]{V}$—characteristic size of the sample. One can introduce for macroscopically inhomogeneous medium the function $\rho(\mathbf{r})$—local conductivity, thus fulfilling relation

$$\mathbf{E}(\mathbf{r}) = \rho(\mathbf{r})\mathbf{j}(\mathbf{r}),$$

Introduced earlier in (2.1.2) effective kinetic coefficient ρ_e is called by "effective resistivity of the composite medium". Generally speaking, ρ_e and $\langle\rho\rangle$ do not coincide. They are same in the obvious case of flat-layered medium. One can instead of using ρ_e—resistivity, utilize σ_e—effective conductivity, which effectively connects averaged over volume values of fields and currents

$$\langle\mathbf{j}\rangle = \sigma_e\langle\mathbf{E}\rangle, \quad \sigma_e = 1/\rho_e. \qquad (2.1.5)$$

In complete analogy one can speak of the other effective kinetic coefficients (EKC) such as: thermal conductivity, thermo-EMF, Young modulus, etc.

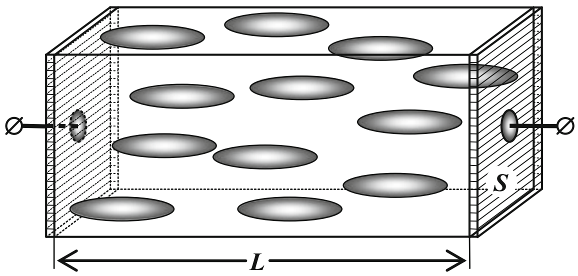
$$\langle\mathbf{q}\rangle = -\kappa_e\langle\nabla T\rangle, \qquad (2.1.6)$$

$$\langle\mathbf{j}\rangle = -\sigma_e\langle\nabla\xi\rangle - \sigma_e\alpha_e\langle\nabla T\rangle, \qquad (2.1.7)$$

where κ_e—EKC of thermal conductivity, σ_e and α_e—EKC of conductivity and thermo-EMF.

It is worthy mentioning EKC, which is different from their specific characteristics of subsequent homogeneous ones. In Fig. 2.4 we show the medium with elongated longitudinally inclusions. Even though locally medium is isotropic effective resistivity is a second rank tensor.

Fig. 2.4 Inhomogeneous medium with elongated longitudinal inclusions



$$\rho = \rho(\mathbf{r}) = \begin{cases} \rho_1, \mathbf{r} \in O_1, \\ \rho_2, \mathbf{r} \in O_2, \end{cases} \tag{2.1.8}$$

Introduction of EKC is connected to the idea that as long as we are able to find them, we are in position to calculate many integral properties of the concrete samples of the medium, for instance, resistance of a sample with arbitrary geometry and connect it to an experimental value.

In some cases EKC could be defined slightly differently, for instance, for $\hat{\sigma}_e$ we can define

$$\hat{\sigma}_e = \frac{\langle \sigma(\mathbf{r})\mathbf{E}^2(\mathbf{r}) \rangle}{\langle \mathbf{E}(\mathbf{r}) \rangle^2}, \tag{2.1.9}$$

This expression immediately follows from (for example [3])

$$\langle \mathbf{E}\mathbf{j} \rangle = \langle \mathbf{E} \rangle \langle \mathbf{j} \rangle, \tag{2.1.10}$$

which is correct provided that we completely neglect boundary effects. Indeed, substituting in left hand side of formula (2.1.10) expression for current density $\mathbf{j} = \sigma\mathbf{E}$, and using in right hand side the fact, that (2.1.5) $\langle \mathbf{j} \rangle = \sigma_e \langle \mathbf{E} \rangle$ we obtain (2.1.9), arriving at a reasonable result that the effective conductivity could be understood as a normalized averaged Joule heat production.

The validity of (2.1.10) (detailed discussion and generalization of (2.1.10) see in [1] could be understood in the following simplified way. Writing the expression for an effective electric field in the following form

$$\mathbf{E}(\mathbf{r}) = \langle \mathbf{E} \rangle - \nabla\varphi(\mathbf{r}), \tag{2.1.11}$$

where potential $\varphi(\mathbf{r})$ corresponds to the field, scattered by inhomogeneities

$$\langle \nabla\varphi(\mathbf{r}) \rangle = 0.$$

The difference between left and right hand sides in (2.1.11) could be transformed into surface integration

$$\langle \mathbf{Ej} \rangle - \langle \mathbf{E} \rangle \langle \mathbf{j} \rangle = \frac{1}{V} \int \mathbf{Ej}\, \mathrm{d}V - \langle \mathbf{E} \rangle \langle \mathbf{j} \rangle = \frac{1}{V} \int \langle \mathbf{E} \rangle \mathbf{j}\, \mathrm{d}V - \langle \mathbf{E} \rangle \langle \mathbf{j} \rangle - \frac{1}{V} \int \nabla \varphi \mathbf{j}\, \mathrm{d}V.$$

First two terms cancel, and the third one yields with the help of $\mathrm{div}\mathbf{j} = 0$ following result:

$$\frac{1}{V} \int \nabla \varphi \mathbf{j}\, \mathrm{d}V = \frac{1}{V} \int \nabla (\varphi \mathbf{j})\, \mathrm{d}V = \frac{1}{V} \int \varphi \mathbf{j}\, \mathrm{d}\mathbf{S}, \tag{2.1.12}$$

which vanishes in the limit $V \to \infty$.

Vanishing of the surface integral in (2.1.12) can be achieved in samples of finite sizes by appropriate boundary conditions and distribution of phases

2.2 Correlation Length and Self-averaging

So far we always assumed that EKC's could be uniquely introduced, if the characteristic length of the sample is large enough. Now we will suggest more rigorous definition of "large enough characteristic size". For this purpose we will introduce correlation length ξ, or correlation radius.

Let $\varphi(\mathbf{r})$—some random physical field, and $\rho(\varphi, \mathbf{r})\mathrm{d}\varphi$ is a probability to find values of φ in interval $(\varphi; \varphi + \Delta\varphi)$ around $\mathbf{r}$. Ergodic hypothesis is the statement that expectation value of a random process can be done as an ensemble integration

$$\langle \varphi \rangle = \frac{1}{V} \int \varphi(\mathbf{r})\, \mathrm{d}\mathbf{r} = \int \varphi \rho(\varphi)\, \mathrm{d}\varphi. \tag{2.2.1}$$

We use S-point moment, and S-point function, or distribution $P_s(\varphi_1, \mathbf{r}_1; \varphi_2, \mathbf{r}_2; \ldots; \varphi_s, \mathbf{r}_s)$. If $S = 2$, and using assumption that random field is homogeneous and isotropic we have

$$P_2(\varphi_1, \mathbf{r}_1; \varphi_2, \mathbf{r}_2) \equiv P_2(\varphi_1, \varphi_2; r), \tag{2.2.2}$$

where $r = |\mathbf{r}_2 - \mathbf{r}_1|$. This function posses following limited boundary properties:

$$P_2(\varphi_1, \varphi_2; r) \to \begin{cases} \delta(\varphi_1 - \varphi_2)\rho(\varphi_1, \varphi_2), & r \to 0, \\ \rho(\varphi_1) \cdot \rho(\varphi_2), & r \to \infty. \end{cases}$$

Introducing autocorrelation function

$$\Gamma(r) = \frac{\langle \varphi(0)\varphi(\mathbf{r})\rangle}{\langle \varphi^2 \rangle} \equiv \frac{\int \varphi_1\varphi_2 P_2(\varphi_1, \varphi_2, r)\, \mathrm{d}\varphi_1 \mathrm{d}\varphi_2}{\int |\varphi^2| \rho(\varphi)\, \mathrm{d}\varphi}, \tag{2.2.3}$$

then

$$\Gamma(r) \to \begin{cases} 1, & r \to 0, \\ 0, & r \to \infty. \end{cases}$$

According to [5] one may define the correlation length and similar different areas of continuous random field $\varphi(\mathbf{r})$, as its characteristic topological signature, or the typical spacial size

$$\xi^2 = \frac{\int r^2 \Gamma(r)\, \mathrm{d}^3 r}{\int \Gamma(r)\, \mathrm{d}^3 r}., \tag{2.2.4}$$

Relatively uniform medium, therefore, in addition to the sizes of different inclusions and distances among them ("microscopic" sizes), possesses yet another characteristic length ξ. Effective properties of the parts of media with sizes $L \gg \xi$ will be the same.

As it is well known, for the Gaussian random field [4, 5]

$$\Gamma(r) \sim \mathrm{e}^{-r/\xi}, \tag{2.2.5}$$

As the appropriate example we will again consider a conducting medium. Uniqueness of σ_e requires, that the average values $\langle \mathbf{j} \rangle$ and $\langle \mathbf{E} \rangle$ in the relationship $\langle \mathbf{j} \rangle = \sigma_\mathrm{e} \langle \mathbf{E} \rangle$ would not depend on the location, where we choose a sample or on random realization of different conducting phases. Condition (2.2.1) signifies the fact that the correlation among their distribution is rather weak. This example will also serve as an indicator of the property which we call self-averaging [2]. We define it in the following way. For arbitrary realization ω of the random $\sigma(r)$ there exists a unique value of σ_e, such that $\langle \mathbf{j} \rangle_\omega = \sigma_\mathrm{e} \langle \mathbf{E} \rangle_\omega$. In other words, σ_e does not depend on ω, and averaging over volume coincides with averaging over ensemble of different realizations (ergodic hypothesis)

References

1. Balagurov BY (1987) Galvanomagnetic properties of inhomogeneous media in a weak magnetic field Sov. Phys JETP 66:1079–1087
2. Bonch-Bruevich V, Zvagin I, Kiper R (1981) Electronic theory of inhomogeneous semiconductors Nauka, M, 384 p (in Russian)
3. Dykhne AM (1970) Contluctivity of a two-dimensional two-phase system Sov. Phys JETP 32:63–64

4. Monin AC, Yaglom AM (1965) Statistical hydromechanics, v.1 Nauka, Moscow 640 p (in Russian)
5. Ziman JM (1979) Models of disorder: the theoretical physics of homogeneously disordered systems. Cambridge University Press, London, 538 p

Chapter 3
Effective Conductivity of Macroscopically Disordered Media

3.1 Double-Sided Estimates of the Effective Kinetic Coefficients

Let us ask a question: what can be learned of the effective kinetic coefficient, if very little is known about the medium characteristics. After all, even for an approximate determination of the effective kinetic coefficient one should have some information on the medium, the concentration of inclusions, their shape, mutual arrangement, etc. It appears that there exists a certain minimum of information that allows obtaining double-sided estimates of the effective kinetic coefficient value which are often referred to as “bounds.” Using additional information on the characteristics of medium, the “bounds” can be narrowed, specifying possible bounds of the effective kinetic coefficient, i.e., the larger information is taken into account, the narrower are the “bounds.”

Consider double-sided restrictions on the effective kinetic coefficients by an example of the effective conductivity σ_e of a double-phase medium with conductivities of its component phases σ_1 and σ_2. For certainty, we will assume $\sigma_1 > \sigma_2$. Evidently, the simplest and at the same time the widest bounds of σ_e will be governed by inequalities

$$\sigma_2 \le \sigma_e \le \sigma_1, \tag{3.1.1}$$

which means that σ_e cannot be larger than maximum conductivity of medium $\sigma_{max} = \sigma_1$ and smaller than minimum $\sigma_{min} = \sigma_2$. The second in complexity and, naturally, a narrower “bound” can be obtained using additional information on the medium, for instance, phase concentration.

Consider a case in Fig. 3.1a with alternation of parallel layers of different phases. We will average the expression $j_x = \sigma(y)E_x$ (direction of axes is evident from Fig. 3.1)

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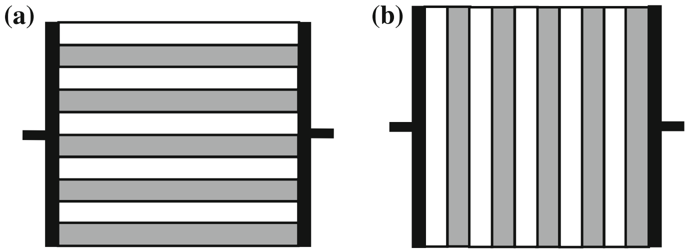

Fig. 3.1 Examples of phase arrangements whereby sample conductivity: **a** is maximum $\sigma_{\max} = \sigma_{[[}$; **b** is minimum $\sigma_{\min} = \sigma_{\perp}$

$$\left\langle \frac{1}{\sigma(y)} j_{\mathrm{x}} \right\rangle = \left\langle \frac{1}{\sigma} \right\rangle j_x = \langle E_x \rangle, \quad \text{whence} \langle j_{\mathrm{x}} \rangle = \left\langle \frac{1}{\sigma} \right\rangle^{-1} \langle E_x \rangle.$$

Besides, $\langle j_x \rangle = \sigma_{\perp}^{\mathrm{e}} \langle E_x \rangle$. Comparing these values, we find $\sigma_{\perp} = \langle 1/\sigma \rangle^{-1}$. In a similar way one can find $\sigma_{||} = \langle \sigma \rangle$, here $\sigma_{\perp}$ and $\sigma_{||}$ are components of the effective conductivity tensor along and across the layers

$$\hat{\sigma}_{\mathrm{e}} = \begin{pmatrix} \sigma_{||} & 0 \\ 0 & \sigma_{\perp} \end{pmatrix}. \tag{3.1.2}$$

In this case $\langle \sigma \rangle = p\sigma_1 + (1-p)\sigma_2$, and $\langle \sigma^{-1} \rangle = p/\sigma_1 + (1-p)/\sigma_2$, where p is phase concentration σ_1. Whence

$$\langle \sigma^{-1} \rangle^{-1} = \frac{\sigma_1 \sigma_2}{p\sigma_2 + (1-p)\sigma_1} \le \sigma_{\mathrm{e}} \le p\sigma_1 + (1-p)\sigma_2 = \langle \sigma \rangle \tag{3.1.3}$$

Inequalities (3.1.3) were first established by Wiener. The left boundary value was found by Voigt, the right—by Reis. Note that for the average isotropic medium the achievement of bounds (3.1.3) is impossible.

The general concept of derivation of double-sided estimates is based on the existence of principle of functional minimum equal in the case of conducting medium to energy dissipation (the Joule heat release):

$$\Phi = \int_V (\mathbf{Ej}) \mathrm{d}V. \tag{3.1.4}$$

In the stationary case $E = -\nabla\varphi$ and, as can be easily shown, from functional minimum (3.1.4) there follows $\operatorname{div} \mathbf{j} = 0$. Indeed, writing down (3.1.4) as

$$\Phi[\sigma, \nabla\varphi] = \int F(\sigma, \nabla\varphi) \mathrm{d}V, F = \sigma(\nabla\varphi)^2, \tag{3.1.5}$$

from the Euler's equation for F

$$\sum_k \frac{\partial}{\partial x_k} \frac{\partial F}{\partial\left(\frac{\partial \varphi}{\partial x_k}\right)} - \frac{\partial F}{\partial \varphi} = 0, \tag{3.1.6}$$

we obtain at once $\operatorname{div} \mathbf{j} = 0$, i.e., those distributions of fields $\mathbf{E}(\mathbf{r})$ and currents $\mathbf{j}(\mathbf{r})$ which satisfy Maxwell's equations and assign minimum to functional Φ (3.1.4). Hence follows a general concept of constructing two-sided estimates—selection from different physical considerations of functions $\mathbf{j}(\mathbf{r})$ and $\mathbf{E}(\mathbf{r})$ (they are called "trial"), so that $\Phi[\sigma, \nabla\varphi]$ (3.1.4) be as low as possible. The application of a variational principle to construction of double-sided estimates (in particular, generalization for the anisotropic case) is given in [6], see also [3], Chap. 6.

Now we derive the relation (3.1.3) in a more general form. For this purpose we will use the previously obtained relation $\langle \mathbf{E} \cdot \mathbf{j} \rangle = \langle \mathbf{E} \rangle \cdot \langle \mathbf{j} \rangle$ (see paragraph 2.1). Taking into account that the average $(\mathbf{E} \cdot \mathbf{j})$ has a minimum on the true values of field $\mathbf{E}$ and assuming the values $\langle \mathbf{E} \rangle$ and $\langle \mathbf{j} \rangle$ as trial values of $\mathbf{E}$ and $\mathbf{j}$, we obtain

$$\langle \mathbf{Ej} \rangle = \langle \mathbf{E} \rangle \langle \mathbf{j} \rangle = \sigma_e \langle \mathbf{E} \rangle^2 = \left\langle \sigma \mathbf{E}^2 \right\rangle \le \langle \sigma \rangle \langle \mathbf{E} \rangle^2, \tag{3.1.7}$$

$$\langle \mathbf{Ej} \rangle = \frac{1}{\sigma_e} \langle \mathbf{j} \rangle^2 = \left\langle \frac{1}{\sigma} \mathbf{j}^2 \right\rangle \le \left\langle \frac{1}{\sigma} \right\rangle \langle \mathbf{j} \rangle^2. \tag{3.1.8}$$

Hence we find the final relation

$$\left\langle \sigma^{-1} \right\rangle^{-1} \le \sigma_e \le \langle \sigma \rangle. \tag{3.1.9}$$

The next in complexity and even narrower "bound" can be obtained for the average isotropic medium. Note that the inequalities (3.1.3) describe in the general case the anisotropic medium, when $\hat{\sigma}_e$ is a tensor. Estimates of σ_e for the isotropic medium are called Hashin–Shtrikman "bounds" [12, 13]. To obtain them, one employs a generalized variational principle and finds for σ_e narrower bounds than those given by the relations (3.1.3). A detailed derivation can be found in the work [32]. In particular, for the two-phase material these bounds are determined by inequalities (at $\sigma_1 > \sigma_2$)

$$\sigma_2 + \frac{p}{1/(\sigma_1 - \sigma_2) + (1-p)/3\sigma_2} \le \sigma_e \le \sigma_1 + \frac{1-p}{1/(\sigma_2 - \sigma_1) + p/3\sigma_1}. \tag{3.1.10}$$

Hashin and Shtrikman showed that the bounds (3.1.10) cannot be improved, if phase concentrations p are assigned. Figure 3.2 shows the region of "borders" for different σ_1 and σ_2 values. The "borders" "work" well at low values of $\frac{\sigma_1}{\sigma_2}$ ratio, at large $\frac{\sigma_1}{\sigma_2}$ values the double-sided restrictions are practically useless.

In the construction of "borders" one can use a more detailed information on the composite than phase concentration and medium isotropy, for instance, information

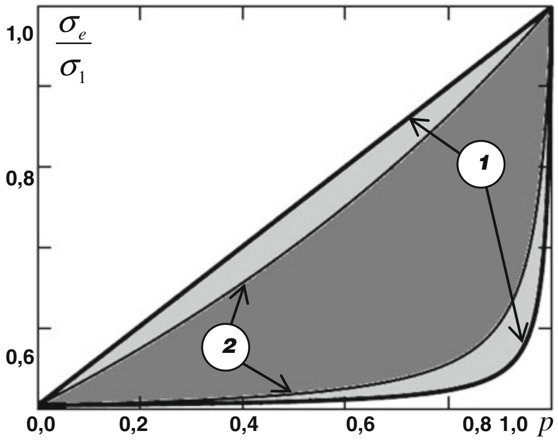

Fig. 3.2 Double-sided restrictions for conductivity: *1* "bound" (3.1.9); *2* Hashin–Shtrikman "bound" (3.1.10)

on the geometry of phase arrangement or the data on three-point correlation function. A review of the respective results is given in [3, 14]. The above-considered variational principle can be extended to the problems of magnetostatics, which allows finding double-sided restrictions for the magnetic field energy and the induction of multicomponent materials [15]. For the case of complex values of phase conductivity (quasi-harmonic case of conductivity on the alternating current) one can also construct the respective "borders" [4, 10]. Their construction is based on the assumption of analyticity of complex conductivity functions.

3.2 Approximations of Maxwell, Garnett, and Bruggeman

The Maxwell approximation. The Maxwell approximation is based on the assumption that concentration of inclusions of one of the phases is low and the inclusions have a correct compact shape, for instance, spherical. Contrary instance is "metal" net in dielectric medium. The conducting phase concentration is low and at the same time the inclusions are not compact.

One can obtain σ_e in the analytical form in the Maxwell approximation only for inclusions of certain shape. The general view of such a shape is a three-axial ellipsoid. Under low concentration is understood such concentration of inclusions $(p \ll 1)$ whereby the effect of one inclusion on the other (neighboring) can be neglected. It means that the problem of distribution of fields and currents can be solved for the case of a single inclusion. The analytical solution of such problem for ellipsoid is well known. Note that the field inside the inclusion in this case proves to be homogeneous. This fact allows finding a good approximation for the effective conductivity in the nonlinear case as well.

Let us consider first the case of spherical inclusions. Let p be concentration of good conducting phase of conductivity σ_1 (for instance, inclusions) in a medium of