
CHAPTER 5

Theory of Heterogeneous Materials

5.1. Introduction

We shall now consider heterogeneous materials that may be conveniently treated from a statistical point of view. We shall specifically discuss the elastic and electrical properties of these materials. By heterogeneous materials we mean here materials in which the macroscopic electric or elastic properties vary from point to point within a material sample. We shall restrict ourselves to cases in which this variation is independent of time.

In a sense, all samples of materials are heterogeneous if we make fine enough measurements. The principal practical application of this chapter, however, is intended for materials in which the variation of material properties is an obvious macroscopic property of the material. We will not consider variations resulting from atomic effects.* For example, we consider here inclusions of one material in another, multiphase material mixtures and polycrystals. In all these cases the composition of these materials may have either an ordered or a random character, but we consider here only the latter case.

5.1.1. Effective Constants

In the introductory chapters of this book we stressed what is meant by a proper description of a continuum problem that has statistical aspects. Although heterogeneous materials were later conveniently described from a statistical point of view, most early investigations were concerned with determining effective constants of such media. A discussion of these constants provides, perhaps, the best physical introduction to the theory of heterogeneous materials.

* For a discussion of atomic effects we refer the reader to Burgess, Ed., *Fluctuation Phenomena in Solids* (1965).

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Statistical continuum theories.

The concept of effective constants is superficially quite intuitive, but under deeper analysis many subtleties appear. On the surface the problem is simply to take a sample of a material within which some material constant varies with position and determine the overall constant of the sample in the same manner that we would if the constant were independent of position within the sample. For example, we consider the problem of determining the Young's modulus E of a material sample.

If Young's modulus is independent of position, we determine it by subjecting a material sample of length l and cross-sectional area A to a tensile force F . We measure the change in length Δl and determine E from the formula

$$E = \frac{F/A}{\Delta l/l} \quad (5-1)$$

If Young's modulus is dependent upon position, we may determine an effective constant E^* in exactly the same manner. We again chose a sample of length l and cross-sectional area A and determine E^* from the equation†

$$E^* = \frac{F/A}{\Delta l^*/l} \quad (5-2)$$

where Δl^* is the change in length of this heterogeneous sample. (We note that E^* determined in this manner will not in general equal \bar{E} where \bar{E} is the volume average value of E in the sample.)

Now having determined E^* in this manner, we hope it will have applicability beyond the confines of this particular experiment. We would certainly hope that E^* would not depend upon the values of A and l that we chose as our sample size. If we cut the sample in four equal parts we would hope that if experiments were made on each sample individually that the value of E^* obtained would be the same in all four samples. It is possible however that this would not be so. In making tests on heterogeneous materials to determine effective constants of general applicability the assumption must always implicitly be made that the samples are in some sense "homogeneous."

† See Section 3.3 for a remark on the connection between this type of definition and an energy-type definition. This point will also be discussed later in this chapter (Secs. 5.1.4, 5.3).

By "homogeneous" in the sense used above we mean *statistically* homogeneous. Further, we mean *statistically homogeneous* in a volume-averaged sense, not in an ensemble-averaged sense. What is meant is twofold. First, all characteristic lengths that appear in a problem of a material under stress must be large compared to a distance, for example, d_M , within which the modulus E undergoes considerable variation about its mean value. Second, loosely speaking, the character of the variations in a volume element of size d_M^3 in one part of the sample must be of the same sort as the variations in another part of the sample. The latter condition is usually met if the sample is uniformly mixed when it is manufactured but if care is not taken gravitational effects, for example, can sometimes introduce nonuniformities.

In the test cited above we would demand that l and $A^{1/2}$ be much larger than d_M . If we wish to use the results obtained here on samples one fourth the size, then

$$\frac{A^{1/2}}{4} \gg d_M, \quad l/4 \gg d_M$$

It is easy to see the difficulty that would arise if $A^{1/2}$ and l were much less than d_M . In one sample E could then be a constant E_1 ; in another, a constant E_2 ; in another, perhaps vary linearly between the values E_3 and E_4 ; and so on. There would be no chance for the variations of E to average out within a single sample and every sample would yield a different value for E^* .

The effective constants determined by the above experiment are also expected to have validity in materials subjected to nonconstant external forces. In this case we must meet the condition that the average stress does not change appreciably over distances large compared to d_M . For the effective constant E^* , determined in the above manner, to be meaningful within a material, the average stress must encounter the same material conditions that were encountered during the determination of E^* . In other words, the stress must be essentially constant in distances over which significant variations of E occur.

In most practical cases the conditions given above are easily realized and the experimenter knows intuitively that if he is using a mixture it must be well mixed within a sample. Unless one is especially aware of this problem, however, there is a tendency to forget that the above conditions may easily be violated in regions of very strong stress

concentration. If the above conditions are violated, then one cannot consider a heterogeneous material by simply replacing E by E^* whenever Young's modulus occurs in the theory of homogeneous materials. In these cases the concept of an effective constant breaks down.

Although we did not wish to complicate the above discussion by stating further conditions it is also necessary in most instances that the sample be statistically isotropic. It should not matter on which faces of the sample we apply forces to measure E^* provided only that all dimensions are large compared to d_M . If the orientation of the sample was important, the concept of an effective constant would be severely limited.

In the classical theory of elasticity we assume the following relation between stress and strain for a homogeneous isotropic elastic body.

$$(5-3) \quad \tau_{ij} = \lambda e_{ii} \delta_{ij} + 2\mu e_{ij}$$

where τ_{ij} is the stress tensor, e_{ij} is the strain tensor, μ is the shear modulus and λ is related to the bulk modulus k , by the relation $k = \lambda + 2/3\mu$. We also have

$$E = \frac{\mu(3\lambda + 2\mu)}{\lambda + \mu}$$

The constants λ and μ may be determined by finding E in the method outlined above and perhaps finding μ in a torsion experiment.

If all characteristic lengths appearing in consideration of the problem of a heterogeneous material under stress are large compared to d_M and the orientation of the sample is unimportant, the assumption is usually made that

$$(5-4) \quad \langle \tau_{ij} \rangle = \lambda^* \langle e_{ii} \rangle \delta_{ij} + 2\mu^* \langle e_{ij} \rangle$$

Here $\langle \tau_{ij} \rangle$ and $\langle e_{ij} \rangle$ denote the stress and strain averaged over a local volume large compared to d_M .[†] λ^* and μ^* are the effective elastic constants determined by experiments identical to those used in the analysis of homogeneous materials. In experiments such as these the characteristic sample lengths are large compared to d_M . We remember that two types of characteristic lengths enter the problem. We must consider characteristic lengths associated with the size of the

[†] In this chapter the angular brackets denote a local volume average. The reader is cautioned not to confuse this notation with the use of angular brackets in the previous chapter where they denoted a time average.

medium under study and we must consider characteristic lengths associated with distances over which the stress and strain field vary appreciably. If either characteristic length of the problem is less than d_M there is no basis for postulating an equation like Eq. 5-4.

We note again that the constants λ^* and μ^* are not equal to $\langle \lambda \rangle$ and $\langle \mu \rangle$, respectively. This may be seen by writing

$$(5-5) \quad \begin{aligned} \lambda(\mathbf{x}) &= \langle \lambda(\mathbf{x}) \rangle + \lambda'(\mathbf{x}) \\ \mu(\mathbf{x}) &= \langle \mu(\mathbf{x}) \rangle + \mu'(\mathbf{x}) \\ e_{ij}(\mathbf{x}) &= \langle e_{ij}(\mathbf{x}) \rangle + e_{ij}'(\mathbf{x}) \\ \tau_{ij}(\mathbf{x}) &= \langle \tau_{ij}(\mathbf{x}) \rangle + \tau_{ij}'(\mathbf{x}) \end{aligned}$$

where $\langle \lambda'(\mathbf{x}) \rangle = \langle \mu'(\mathbf{x}) \rangle = \langle e_{ij}'(\mathbf{x}) \rangle = \langle \tau_{ij}'(\mathbf{x}) \rangle = 0$. Again the brackets denote a local volume average.

Substituting the expressions given in Eq. 5-5 into Eq. 5-3 and taking a local volume average, we find

$$(5-6) \quad \langle \tau_{ij} \rangle = \bar{\lambda} \langle e_{ii} \rangle \delta_{ij} + \langle \lambda' e_{ii} \rangle \delta_{ij} + 2\mu \langle e_{ij} \rangle + 2\langle \mu e_{ij}' \rangle$$

In general the terms $\langle \lambda' e_{ii} \rangle$ and $\langle \mu' e_{ij}' \rangle$ are not zero and hence to make Eqs. 5-4 and 5-6 compatible, λ^* and μ^* cannot be equal to $\langle \lambda \rangle$ and $\langle \mu \rangle$, respectively. The relationship that does exist between λ^* and μ^* and $\langle \lambda \rangle$, $\langle \mu \rangle$, $\langle \lambda' e_{ii} \rangle$ and $\langle \mu' e_{ij}' \rangle$ requires discussion of a mathematical nature and we shall defer this point until later in the chapter. In this introduction we need to note only the fact that some relationship does exist.

As a last remark we note that in this chapter we shall only consider effective constants for heterogeneous materials that are statistically homogeneous and isotropic. We shall not consider here what must be done to treat materials that do not satisfy this condition. (If, however, the material properties vary "slowly" with position, then it is possible to define local effective constants $\langle \lambda \rangle$ and $\langle \mu \rangle$ that vary with position.) In the statistical analyses that follow, we shall sometimes treat aspects of the statistically nonhomogeneous problem which need not be discussed in terms of effective constants.

5.1.2. Use of Volume Fractions in Determining Effective Constants

When attempting to determine constants like E^* , λ^* , and μ^* for an inclusion of one material within another or a mixture of two materials,

the most easily measurable quantity is the volume fraction of each material. It is thus most natural to attempt to find E^* , λ^* , and μ^* in terms of volume fractions.

Unfortunately these constants are not determined by the volume fractions alone but depend upon the geometry associated with the material mixture. To see this intuitively consider the following limiting cases given in Fig. 5-1.

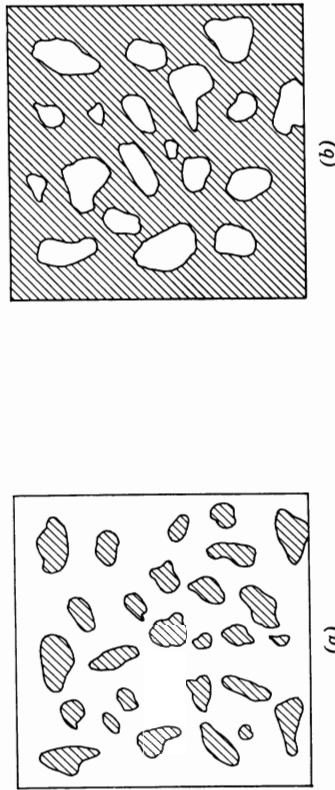


Fig. 5-1. Limiting types of inclusions. *a.* Young's modulus of inclusion E_1 , Young's modulus of matrix E_2 , $E_1 \gg E_2$. *b.* Young's modulus of inclusion E_2 , Young's modulus of matrix E_1 , $E_1 \gg E_2$.

We suppose that the sample in Fig. 5-1*a* is composed of a matrix material with Young's modulus E_2 and an inclusion with Young's modulus E_1 , where $E_1 \gg E_2$. We think of the matrix as being composed of a soft material like lead and the inclusion as being composed of a hard material like steel. The sample size is taken to be very large compared to a characteristic inclusion size or average distance between inclusions. The inclusions are spread randomly throughout the sample and the sample is constructed so that it appears the same when viewed from any angle. In statistical language the sample is statistically homogeneous and isotropic. The second sample has similar properties except that in this case the matrix material has the Young's modulus E_1 and the inclusion the Young's modulus E_2 . We choose the volume fractions in both samples to be 50% matrix and 50% inclusion.

We now wish to determine E^* for both samples by using the simple tension experiment described above. In the first case, the Young's modulus of the inclusion is much greater than the Young's modulus of

the matrix. We may think of steel pellets in a lead matrix. Under tension the steel will provide resistance to elongation but since the matrix provides continuous paths of lead from one face of the sample to the other, the lead will "provide" more of the resistance to elongation. In the second case, the Young's modulus of the matrix is much greater than the Young's modulus of the inclusion. We expect here that the resistance that the sample gives to elongation will again be governed principally by the matrix. In this case the steel will "provide" more of the resistance to elongation.

The reader should note that the above statements are meant to appeal to only intuition and in no sense provide proof. If the reader does not find the above statements convincing, he might consider for a moment a steel-rubber combination rather than a steel-lead combination.

In the above samples the volume fractions of lead and steel were the same in each case. Since E^* will be different in the two cases we conclude that volume fractions are not sufficient to determine E^* for a mixture. Evidently the specific geometrical arrangement is also important in determining E^* . The effect is certainly not limited to the inclusion-matrix concept. We would expect, for example, that if lead and steel were mixed in equal proportions by volume in such a manner that neither could be considered to be an inclusion in the matrix of the other that a third value of E^* would be obtained.

The possible ways in which two materials may be mixed together in equal volume proportions is countless. To describe the geometrical arrangement when the mixture is random we rely on the concept of correlation functions or, more generally, probability density functions. The volume fraction of material 1 and material 2 may be represented by the following probability density function

$$P_1[E(\mathbf{x})] dE(\mathbf{x})$$

defined roughly as the probability that we find the material with Young's modulus E at point \mathbf{x} . Since $E(\mathbf{x})$ may take on only two values, E_1 and E_2 , we may write

$$(5-7) \quad P_1[E(\mathbf{x})] = v_1 \delta[E(\mathbf{x}) - E_1] + v_2 \delta[E(\mathbf{x}) - E_2]$$

The Dirac delta function indicates that the probability density function is nonzero only when $E(\mathbf{x})$ is equal to E_1 or E_2 . v_1 and v_2 are the volume fractions of material 1 and 2, respectively. The probability that the

value of $E(\mathbf{x})$ is E_1 at point \mathbf{x} is obtained by evaluating the integral

$$(5-8) \quad P(E_1) = \int_{E_1-\Delta E}^{E_1+\Delta E} P_1[E(\mathbf{x})] dE(\mathbf{x})$$

for small values of ΔE ; that is, in the neighborhood of E_1 . The result is

$$(5-9) \quad P(E_1) = v_1$$

In other words, we have the obvious result that the probability of finding the value E_1 at some point \mathbf{x} is equal to the volume fraction of that material.

To introduce the concept of the probability density function with the attendant delta functions is of course pointless to obtain the result given in Eq. 5-9. The probability density concept is necessary, however, for obtaining more information about the geometrical arrangement of the mixture. More information about the geometrical arrangement is given by the two-point probability density function

$$P_2[E(\mathbf{x}_1), E(\mathbf{x}_2)] dE(\mathbf{x}_1) dE(\mathbf{x}_2)$$

defined roughly as the probability that the value of E at \mathbf{x}_1 is $E(\mathbf{x}_1)$ and the probability of E at \mathbf{x}_2 is $E(\mathbf{x}_2)$. The relation between P_1 and P_2 is

$$(5-10) \quad P_1[E(\mathbf{x}_1)] dE(\mathbf{x}_1) = \int_{\text{all values of } E(\mathbf{x}_2)} P_2[E(\mathbf{x}_1), E(\mathbf{x}_2)] dE(\mathbf{x}_1) dE(\mathbf{x}_2)$$

The probability density function P_2 indicates how quickly the value of E changes with separation $|\mathbf{x}_2 - \mathbf{x}_1|$. From $P_2[E(\mathbf{x}_1), E(\mathbf{x}_2)]$, for example, we can determine the probability that $E(\mathbf{x}_2)$ will have the value E_1 at point \mathbf{x}_2 if it has the value E_1 at point \mathbf{x}_1 . The correlation function $R(\mathbf{x}_1, \mathbf{x}_2)$, defined as

$$(5-11) \quad R(\mathbf{x}_1, \mathbf{x}_2) = \frac{E(\mathbf{x}_1)E(\mathbf{x}_2)}{E(\mathbf{x}_1)E(\mathbf{x}_2)} = \iint E(\mathbf{x}_1)E(\mathbf{x}_2)P_2[E(\mathbf{x}_1), E(\mathbf{x}_2)] dE(\mathbf{x}_1) dE(\mathbf{x}_2)$$

is a measure of this type of relatedness between the value of E at point \mathbf{x}_1 and the value of E at point \mathbf{x}_2 . We also note that since the statistical characteristics of a material sample are taken here to be the same in all parts of the sample and are independent of orientation, $R(\mathbf{x}_1, \mathbf{x}_2)$ depends only upon $|\mathbf{r}|$ where $\mathbf{r} = \mathbf{x}_2 - \mathbf{x}_1$.

Beyond knowing the volume fractions v_1 and v_2 of a mixture of two materials the next piece of information that is commonly sought is a correlation function such as $R(|\mathbf{r}|)$. Of course, the volume fraction and $R(|\mathbf{r}|)$ alone do not completely characterize the geometry and it is easy to imagine that an infinite number of higher-order correlation functions are required for a complete specification of the geometry. In fact, E^* depends upon the volume fractions of materials and all correlation functions describing the geometry of the mixture.† In practice we cannot of course know all the correlation functions describing the geometry but we can hope to measure or predict the lower-order correlation functions upon which E^* often strongly depends.

Having made the foregoing statement, however, we must point out to the reader that most of the work to date on the determination of effective constants has been done solely in terms of volume fractions. This is true from both a measurement and a theoretical point of view. The measurement of correlation functions is very tedious and there is virtually no theory to guide one in predicting correlation functions for a given mixing process. We shall discuss what little has been accomplished later in this chapter.

5.1.3. Electrostatic Effective Constants—Tensor Permittivity

The effective constants that we have discussed above are for elastic media that are locally isotropic; that is, they obey a stress-strain relation like that given in Eq. 5-3. The counterpart of this local isotropy in electrostatic problems is the relation

$$(5-12) \quad \mathbf{D}(\mathbf{x}) = \epsilon(\mathbf{x})\mathbf{E}(\mathbf{x})$$

where $\mathbf{D}(\mathbf{x})$ is the electric displacement, $\mathbf{E}(\mathbf{x})$ is the electric field, and $\epsilon(\mathbf{x})$ is the variable permittivity in the medium. A very important heterogeneous medium that we frequently encounter is the polycrystal. Often the individual crystal is not locally isotropic and Eqs. 5-3 and 5-12 must be replaced by a more general relationship. In this introduction we will briefly consider the generalization of Eq. 5-12 since the mathematics is simpler than in the elastic case that requires two

† For exactness we note that E^* depends in general upon the joint moments involving E and another constant like μ , not just on the moments of E alone.

we have upon averaging

$$(5-18) \quad \langle \epsilon_{ij} \rangle = \langle \epsilon_{ij} \rangle \langle E_j \rangle + \langle \epsilon'_{ij} E'_j \rangle$$

If the crystals in the polycrystal are oriented at random then the off-diagonal terms of $\langle \epsilon_{ij} \rangle$ are zero and we find

$$(5-19) \quad \langle \epsilon_{ij} \rangle = \frac{1}{3} (\langle \epsilon_{11} \rangle + \langle \epsilon_{22} \rangle + \langle \epsilon_{33} \rangle) \delta_{ij} = \frac{1}{3} \langle \epsilon_{11} \rangle \delta_{ij}$$

On the average $\langle D_i \rangle$ cannot have a component in a direction other than the direction of $\langle E_i \rangle$ since there is no reason to prefer the negative or positive directions for $\langle D_i \rangle$ along any other axis. For example, suppose $\langle E_i \rangle$ was directed along the z axis; i.e., $\langle E_3 \rangle \neq 0$, $\langle E_1 \rangle = \langle E_2 \rangle = 0$. There is no difficulty in stating that $\langle D_3 \rangle \neq 0$ since $\langle E_3 \rangle$ defines a sense along the "three" axis. If, however, we say that $\langle D_1 \rangle$ or $\langle D_2 \rangle \neq 0$ and the crystals are oriented in a random manner we have no physical reason for stating that, for example, $\langle D_1 \rangle$ should lie in the direction of the positive x axis rather than the negative x axis. We can only conclude that it must be zero. Finally we note that $\langle \epsilon'_{ij} E'_j \rangle$ must be proportional to the electric field since the equations are linear. Equation 5-18 may thus be written in the form

$$(5-20) \quad \langle D_i \rangle = [\frac{1}{3} \langle \epsilon_{11} \rangle + \epsilon^*] \langle E_i \rangle = \epsilon^* \langle E_i \rangle$$

where $\langle \epsilon'_{ij} E'_j \rangle = \epsilon^* \delta_{ij} \langle E_j \rangle$ and ϵ^* depends upon the detailed geometric arrangement of the crystals within the polycrystal.

As we shall see later in the chapter the dependence on the geometry of ϵ^* in the polycrystal case may occur even in the limit of small deviations from local isotropy. This is contrasted to the locally isotropic case in which the geometric effects (beyond volume fractions) may be shown to become progressively less important as deviation from the average permittivity approaches zero.

5.1.4. Definition of Effective Constants Using the Energy Density

The effective permittivity ϵ^* has been defined in Eq. 5-16 by the relation

$$(5-16) \quad \langle D_i \rangle = \epsilon^* \langle E_i \rangle$$

The effective elastic constants have been defined in Eq. 5-4 by the relation

$$(5-4) \quad \langle \tau \rangle_{ij} = \lambda^* e_{ij} \delta_{ij} + 2\mu^* \langle e_{ij} \rangle$$

constants. If the reader prefers not to think in electrical terms, he might consider the medium to have a variable heat conductivity wherein Eq. 5-12 is replaced by

$$(5-13) \quad \mathbf{q}(\mathbf{x}) = k(\mathbf{x}) \nabla T(\mathbf{x})$$

where $\mathbf{q}(\mathbf{x})$ is the heat flux vector, $k(\mathbf{x})$ is the conductivity, and $T(\mathbf{x})$ is the temperature.

If the local properties of the medium are not isotropic, it is often appropriate to replace Eq. 5-12 by the tensor relation

$$(5-14) \quad D_i(\mathbf{x}) = \epsilon_{ij}(\mathbf{x}) E_j(\mathbf{x})$$

where $\mathbf{D}(\mathbf{x})$ and $\mathbf{E}(\mathbf{x})$ retain their original meanings but the scalar permittivity $\epsilon(\mathbf{x})$ must be replaced by the tensor permittivity $\epsilon_{ij}(\mathbf{x})$. In the isotropic case the electric displacement existed only in the direction of the electric field. Equation 5-14, however, allows the possibility of the displacement field existing in a direction that is different from the electric field. For example, if $E_j(\mathbf{x})$ only has a component in the $j = 3$ direction, $D_i(\mathbf{x})$ has components in all three directions

$$(5-15) \quad \begin{aligned} D_1(\mathbf{x}) &= \epsilon_{13}(\mathbf{x}) E_3(\mathbf{x}) \\ D_2(\mathbf{x}) &= \epsilon_{23}(\mathbf{x}) E_3(\mathbf{x}) \\ D_3(\mathbf{x}) &= \epsilon_{33}(\mathbf{x}) E_3(\mathbf{x}) \end{aligned}$$

provided $\epsilon_{33}(\mathbf{x})$ is not zero for $i = 1, 2, 3$.

Although the local properties of the medium are not isotropic, the macroscopic properties of the medium are expected to be isotropic. In a polycrystal we will assume here that the crystals are oriented at random and thus if we average a quantity over a volume that contains many crystals, we expect the result to be independent of orientation. Exactly as in the case of a medium that is locally isotropic we need define only one effective constant ϵ^* , given by the relation

$$(5-16) \quad \langle D_i \rangle = \epsilon^* \langle E_i \rangle$$

Note again that ϵ^* may only be defined if $\overline{E_i}(\mathbf{x})$ is essentially constant over volumes of space that contain many crystals.

If we rewrite Eq. 5-14 using the definitions

$$(5-17) \quad \begin{aligned} D_i(\mathbf{x}) &= \langle D_i \rangle + D'_i(\mathbf{x}) \\ E_i(\mathbf{x}) &= \langle E_i \rangle + E'_i(\mathbf{x}) \\ \epsilon_{ij}(\mathbf{x}) &= \langle \epsilon_{ij} \rangle + \epsilon'_{ij}(\mathbf{x}) \end{aligned}$$

These constants could alternatively have been defined by the energy relations

$$(5-20) \quad \frac{\epsilon^* \langle E_i \times E_i \rangle}{2} = \frac{1}{2} \langle E_i D_i \rangle$$

and

$$(5-21) \quad \frac{1}{2} \lambda^* \langle e_{ij} \rangle \langle e_{ij} \rangle \delta_{ij} + \frac{1}{2} [2\mu^* \langle e_{ij} \rangle \langle e_{ij} \rangle] = \frac{1}{2} \langle \lambda e_{ij} e_{ij} \rangle \delta_{ij} + \langle 2\mu e_{ij} e_{ij} \rangle$$

We pointed out in Chapter 3 (footnote, below Eq. 3-151) that the definitions in Eq. 5-16 and Eq. 5-20 are equivalent, since $\langle E_i' D_i' \rangle = 0$. A similar type proof will establish the equivalence of the definitions given in Eq. 5-4 and 5-21, since $\langle e_{ij} \tau_{ij}' \rangle = 0$. We shall use the two definitions interchangeably in the remainder of the chapter.

5.1.5. Two Simple Physical Models

Because of the difficulty of theoretically and experimentally determining the effect of geometry on the effective constants of a medium a considerable amount of effort has been directed to determining bounds for the effective constants in terms of volume fractions (see Hashin, 1964, for appropriate references) and more recently in terms of low-order correlation functions (see *Transactions of the Rheology Society*, 1965, Pt. 9, No. 1). Later in the chapter we shall show how the bounds may be derived from variational principles (a preliminary discussion was already given in Chapter 3). Here we should like to consider two simple physical models which are sometimes taken as limiting cases of the many geometrical arrangements possible for a homogeneous isotropic mixture of dissimilar materials. The models themselves are not isotropic but they give some indications of limiting behavior of isotropic arrangements. In order to keep the example as simple as possible we consider initially a mixture of two materials and analyze the electrical permittivity case.

The limiting cases that we wish to consider are most easily described by referring to Fig. 5-2a and b. We consider an infinite number of infinite two-dimensional slabs with variable thicknesses. We suppose the cross-hatched slabs have permittivity ϵ_1 and the plain slabs have permittivity ϵ_2 . We construct our samples by alternately placing one

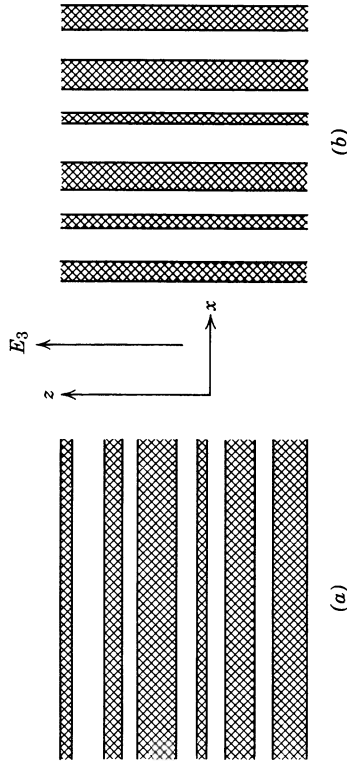


Fig. 5-2. Infinite slab models of a random medium.

type of slab upon the other as indicated in the diagram. The slab thicknesses are chosen at random. The permittivity ϵ thus varies in a random manner in one dimension as a result of the random slab thicknesses. A typical pattern for the permittivity of the medium represented by Fig. 5-2a is given as a function of z in Fig. 5-3. A similar pattern would be obtained by considering the variation of ϵ in the x direction in Fig. 5-2b. Both material samples are, of course, statistically the same; they only differ in their orientation to the z axis.

We suppose that an electric field E_3 is applied to the geometrical arrangements given in Figs. 5-2a and 5-2b. We wish to calculate ϵ^* in both cases, denoted for convenience by ϵ_a^* and ϵ_b^* , respectively. We note again that the samples are not statistically isotropic and thus the effective permittivity depends upon orientation. We wish to

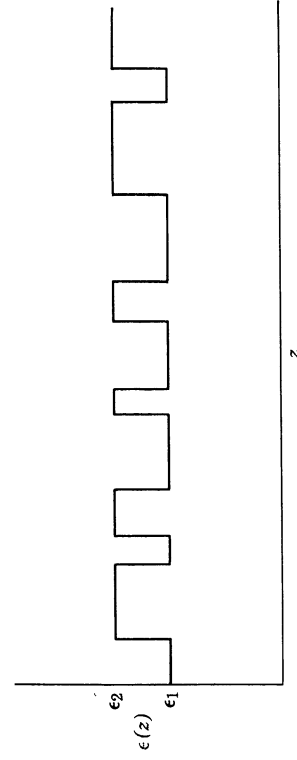


Fig. 5-3. One-dimensional permittivity pattern.

consider the behavior of these two cases, however, as rough limiting behavior possibilities of statistically isotropic material mixtures.

Let us consider the calculation of ϵ_a^* . In this case, the variables are independent of \mathbf{x} . We note from either physical reasoning or reference to the governing equation

$$\frac{\partial}{\partial z} \epsilon(z) E(z) = 0$$

that the displacement

$$(5-22) \quad D(z) = \epsilon(z) E(z)$$

is equal to a constant. (In terms of a heat-conductivity problem this means that the flow of heat q is constant in the z direction; an obvious fact since q cannot depend upon x or y and there are no sinks or sources to collect or emit heat.) We call this constant D and, since the average of a constant is just the constant itself, we note that $D = \langle D \rangle$. From Eq. 5-22, we then find

$$(5-23) \quad E(z) = \langle D \rangle / \epsilon(z)$$

If we now take the volume average of both sides of Eq. 5-23, we find

$$(5-24) \quad \langle E(z) \rangle = \langle D \rangle \langle 1/\epsilon(z) \rangle$$

The defining equation for ϵ_b^* is

$$(5-25) \quad D = \epsilon_a^* E$$

and thus a comparison of Eqs. 5-24 and 5-25 yields

$$(5-26) \quad \epsilon_a^* = \frac{1}{\langle 1/\epsilon(z) \rangle}$$

The average $\langle 1/\epsilon(z) \rangle$ may be written in terms of volume fractions v_1 and v_2 as

$$(5-27) \quad \left\langle \frac{1}{\epsilon(z)} \right\rangle = \frac{v_1}{\epsilon_1} + \frac{v_2}{\epsilon_2}$$

where v_1 is the fraction of volume in the sample occupied by one material (say the cross-hatched material) with permittivity ϵ_1 and v_2 in the fraction of volume occupied by the other material with permittivity ϵ_2 .

The reader will note that this is just the type of formula that is derived in elementary circuit theory for the effective resistance if a voltage is put across a number of resistances in parallel.

The determination of ϵ_b^* proceeds even more directly. In this case the electric field is the same constant in each phase of the material. We have

$$(5-28) \quad \langle E(x, z) \rangle = \langle E \rangle$$

The displacement is a function of x since ϵ is here a function of x . All the variables are independent of z . Thus

$$(5-29) \quad D(x) = \epsilon(x) \langle E \rangle$$

Averaging Eq. 5-29, we find

$$(5-30) \quad \langle D(x) \rangle = \langle \epsilon(x) \rangle \langle E \rangle$$

From the defining relation

$$\langle D \rangle = \epsilon_b^* \langle E \rangle$$

we thus find here that

$$(5-31) \quad \epsilon_b^* = \langle \epsilon(x) \rangle$$

The same results (Eq. 5-26 and Eq. 5-31) would have been obtained if instead of two-phase materials we had considered n -phase materials. That is, we could have made composite materials from an infinite number of two-dimensional slabs in which a percentage v_1 of the slabs had permittivity ϵ_1 , a percentage v_2 had permittivity ϵ_2, \dots , and a percentage v_n had permittivity ϵ_n . In fact, we could let $n \rightarrow \infty$ and find the same answers for ϵ_a^* and ϵ_b^* . We could have considered in the first case a material sample for which ϵ was a random function of z and in the second case a material sample for which ϵ was a random function of x . In the latter case ϵ could have taken any value between 0 and ∞ , provided only that the integral

$$\int_0^{\infty} P_1(\epsilon) d\epsilon$$

was equal to unity, where $P_1(\epsilon) d\epsilon$ is the probability that the material has a value of ϵ between ϵ and $\epsilon + d\epsilon$.

We have shown in Chapter 3, using variational principles, that for a statistically homogeneous isotropic medium

$$(5-32) \quad \frac{1}{\langle 1/\epsilon \rangle} \leq \epsilon^* \leq \langle \epsilon \rangle$$

The relationship holds for the case of continuous variation of ϵ or for the special case of an n -phase material. The relationship was obtained using only a knowledge of volume fractions. Better bounds may be obtained for the case of an n -phase material, as we shall discuss in a moment, but it appears that for the general case in which all values of permittivity are permitted Eq. 5-32 is the most we can say about the range of ϵ^* from just a consideration of volume fractions.

Since the material geometries given in Fig. 5-2 yield the limiting values $1/\langle 1/\epsilon \rangle$ and $\langle \epsilon \rangle$ for Figs. 5-2a and 5-2b, respectively, we may hope that in some sense these geometries represent the limiting behavior of geometries that could exist in a statistically homogeneous and isotropic material. The first case (Fig. 5-2a) indicates a geometrical arrangement in which it is necessary that an electric field path pass sequentially through the entire range of permittivity values. There is no possibility of the electric field path passing through a continuous region with only one value of permittivity as in Fig. 5-2b. Moreover, the geometrical arrangement in Fig. 5-2a tends to emphasize the behavior of regions with low values of permittivity. This may be seen from Eqs. 5-26 and 5-27 in the two-phase case where

$$(5-33) \quad \epsilon_a^* = \frac{1}{(v_1/\epsilon_1) + (v_2/\epsilon_2)}$$

In the limit $\epsilon_2/\epsilon_1 \gg 1$ (v_1 and v_2 of the same order)

$$(5-34) \quad \epsilon_a^* \approx \frac{\epsilon_1}{v_1}$$

A statistically isotropic material that corresponded to the limit of Fig. 5-2a would thus tend to make regions of low permittivity readily accessible and regions of high permittivity (through which the field would normally tend to pass) relatively inaccessible. An extreme example of such a material would be to form a material from discrete fragments of all sizes such that in each fragment the outer portion of the fragment had low values of permittivity and the inner portions had high values of permittivity. In this case, since low permittivity volumes

would have a larger surface area than high permittivity volumes electric field paths would tend to pass through both high and low permittivity regions. On the other hand if the surface availability of both low and high permittivity regions were equal the electric field would tend to pass through regions of high permittivity with a consequent high effective permittivity.

In the second case, paths are available for the electric field that lie entirely in regions of high permittivity or entirely in regions of low permittivity. In the two-phase case

$$(5-35) \quad \epsilon_b^* = v_1\epsilon_1 + v_2\epsilon_2$$

Thus if $\epsilon_2 \gg \epsilon_1$ (and v_1 and v_2 are of the same order)

$$(5-36) \quad \epsilon_b^* \approx v_2\epsilon_2$$

This geometrical arrangement tends to emphasize the behavior of regions with high permittivity. An extreme example of such a geometry for a statistically isotropic medium would be just the inverse of material constructed above. In this case we would construct fragments with an outer coating of high permittivity and an inner core of low permittivity. In this medium the electric field path would tend to lie principally in regions of high permittivity.

When applying these limiting ideas to specific geometrical arrangements great care must, of course, be taken. For example, if the material has permittivity fluctuations that are small and thus all values of the permittivity lie in the neighborhood of the mean value the above limits are never appropriate. In this case we will show later in the chapter that the formula for ϵ^* is always

$$(5-37) \quad \epsilon^* = \langle \epsilon \rangle - \frac{1}{3} \frac{\langle \epsilon'^2 \rangle}{\langle \epsilon \rangle}$$

where $\langle \epsilon'^2 \rangle$ is the mean square fluctuation in permittivity. One could interpret this result to indicate a tendency for the electric field paths to lie in regions of high permittivity but the tendency is certainly not overwhelming.

5.1.6. *n*-Phase Materials

In the special case of an n -phase material or the case when the permittivity takes on continuous values but lies between two finite

values ϵ_m and ϵ_n , Hashin and Shtrikman (1962) have shown that better bounds may be derived in terms of volume fractions than those given in Eq. 5-32. For example, they have shown that for a statistically homogeneous and isotropic two-phase medium that ϵ^* is bounded in the following manner

$$(5-38) \quad \epsilon_1 + \frac{v_2}{1/(\epsilon_2 - \epsilon_1) + v_1/3\epsilon_1} \leq \epsilon^* \leq \epsilon_2 + \frac{v_1}{1/(\epsilon_1 - \epsilon_2) + v_2/3\epsilon_2} \quad (\epsilon_2 > \epsilon_1)$$

This result has been derived in Chapter 3 and will be discussed again later in this chapter.

As Hashin and Shtrikman point out it is particularly interesting that the bounds given in Eq. 5-38 correspond to two different geometric arrangements for which an exact determination of ϵ^* is possible. Consider a material made up of composite spheres of all different sizes so arranged that the void (air volume/sphere volume) ratio approaches zero. A composite sphere is composed of an inner core of radius r_a and permittivity ϵ_a and an outer shell extending from radius r_a to r_b and having a permittivity ϵ_a such that $r_a/r_b = \alpha$ (a constant). The total volume of each sphere is $\frac{4}{3}\pi r_b^3$ and thus the volume fractions v_a and v_b are

$$v_a = \left[\frac{r_a}{r_b} \right]^3 \quad \text{and} \quad v_b = 1 - \left[\frac{r_a}{r_b} \right]^3$$

Hashin and Shtrikman (1962) show that the effective permittivity of such a two-phase material is

$$(5-39) \quad \epsilon^* = \epsilon_b + \frac{v_a}{1/(\epsilon_a - \epsilon_b) + v_b/3\epsilon_b}$$

They do this in a very ingenious manner. They show that if one composite sphere is imbedded in a strictly homogeneous medium with permittivity ϵ^* given by Eq. 5-39 then for a uniform field, the field on the surface of the composite sphere is the same as it would be if the sphere was not there. They reason then that if this holds for one sphere it will hold for two spheres or n spheres and that eventually the entire homogeneous medium with permittivity ϵ^* may be replaced by the composite medium with no change in the average field. Hence, the effective permittivity of the composite sphere medium is given by Eq. 5-39.

Depending upon whether or not ϵ_a/ϵ_b is greater or less than 1, Eq. 5-39 may be made to correspond to either the upper or lower bound of Eq. 5-38. We obtain an upper bound for the effective permittivity when $\epsilon_b > \epsilon_a$; that is when the composite sphere is made of an inner core of low permittivity material and an outer core of high permittivity material. Based upon our previous discussion we expect this case to have a higher effective permittivity than the reverse possibility since in this case more paths through high permittivity material are available to the electric field than if the sphere shells were of low permittivity material. If the sphere shells were of low permittivity material every electric field path must pass through low permittivity material with a consequent reduction of the effective permittivity.

5.1.7. The Self-Consistent Approximation

When we have a statistically homogeneous and isotropic material composed of n phases whose component geometries are not too irregular, we may determine an effective constant for the material by a consistency argument. This approach has been developed in elastic problems by Budiansky (1965) and Hill (1965), and we will outline Budiansky's type of treatment in terms of the simpler dielectric problem. The reader is also referred to Landauer (1952) and Kerner (1956) for similar-type analyses.

In general we define ϵ^* by the relation

$$(5-40) \quad \langle D_3 \rangle = \epsilon^* \langle E_3 \rangle$$

where $\langle E_3 \rangle$ is a constant field in the z direction. We may also write

$$(5-41) \quad U = \frac{1}{2} \epsilon^* \langle E_3 \rangle^2 = \frac{1}{2} \langle D_3 \rangle \langle E_3 \rangle$$

where U is the energy/unit volume. (See Eq. 5-20.) If we rewrite Eq. 5-41 in the form

$$(5-42) \quad U = \frac{1}{2V} \int \langle E_3 \rangle \epsilon_N E_3 dV + \frac{1}{2V} \int \langle E_3 \rangle \langle D_3 \rangle - \epsilon_N E_3 dV$$

(where the subscript N denotes the N th phase), then by explicitly considering the other $N - 1$ phases, we find

$$(5-43) \quad U = \frac{\epsilon^*}{2} \langle E_3 \rangle^2 = \frac{\langle E_3 \rangle^2}{2} \left[\epsilon_N + \sum_{i=1}^{N-1} p_i \left(1 - \frac{\epsilon_N}{\epsilon_i} \right) \frac{\langle D_{3i} \rangle}{\langle E_3 \rangle} \right]$$

where p_i is the volume fraction of the i th phase and D_{3i} is the average value of D_3 in the i th phase.

There are no approximations in Eq. 5-43. For this expression to be useful, however, we must determine $\langle D_{3i} \rangle$. In the self-consistency approximation $\langle D_{3i} \rangle$ is determined by assuming that the i th inclusion is immersed in a continuous matrix of the other $N - 1$ phases; the matrix having a constant dielectric constant ϵ^* . If the inclusion is assumed to have some average shape, $\langle D_{3i} \rangle$ may then be found. If the shape is assumed spherical, then we find (see Stratton, 1941)

$$(5-44) \quad \langle D_{3i} \rangle = \frac{3\epsilon_i \epsilon^* \langle E_3 \rangle}{\epsilon_i + 2\epsilon^*}$$

If the n phases are roughly symmetric and if we assume all inclusions are roughly spherical, we find

$$(5-45) \quad \epsilon^* = \left[\epsilon_N + \sum_{i=1}^{N-1} p_i \left(1 - \frac{\epsilon_N}{\epsilon_i} \right) \frac{3\epsilon_i \epsilon^*}{\epsilon_i + 2\epsilon^*} \right]$$

This expression may be used to find ϵ^* .

In the limit of small perturbations, this formula yields the exact result given in Eq. 5-37. In the elastic case this relation was noted to lie within bounds that are the analog of those given in Eq. 5-32. Similar reasoning should show that Eq. 5-45 lies within the bounds given in Eq. 5-32.

It is not clear at present whether or not this procedure may be reasonably extended to irregular geometries (except if $p_i \ll 1$ for all except one component). Since Eq. 5-43 is correct independently of the detailed geometry, it is certainly worth investigating the relation between $\langle D_{3i} \rangle$ and the geometry of the i th phase. If this is done, however, a more explicitly statistical formulation will probably be necessary.

5.1.8. Dilute Suspensions

As a final remark in this introductory section we note that one limiting case of a two-phase material has received considerable attention in the literature. This is the case of dilute suspensions, or what is often termed small concentration theory. Here a small percentage of one material is considered as an inclusion in the matrix of another material. Numerous references to work in this area are given

by Hashin (1964) and it appears that one of the earliest investigations was by Einstein (1906) in his studies of Brownian motion. The analysis just given for the self-consistent approximation may also be utilized to treat this problem.

This particular limit is easy to handle since the effects of each inclusion may be considered individually. Since the percentage of inclusions is small each included particle may be considered to lie in an infinite matrix of the imbedding material. In the electrostatic

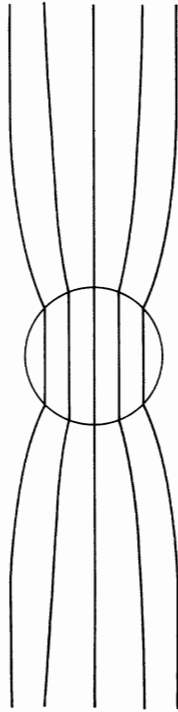


Fig. 5-4. Small concentration theory—field about a single inclusion (see Stratton, J., *Electromagnetic Theory*, McGraw-Hill, 1941, p. 207).

problem the electric field in the neighborhood of the particle may be solved as a straightforward boundary value problem, if the particle geometry is not too complicated. In Fig. 5-4 we show how the electric field would look in the neighborhood of a sphere with permittivity ϵ_1 in a matrix with permittivity ϵ_2 where $\epsilon_1 > \epsilon_2$. The formula for the electric field is derived in Stratton (1941).

From a knowledge of the solution for the boundary value problem we may determine the difference between the energy of the field in the presence of the inclusion and the energy of the field in the absence of the inclusion. Let us term this energy $\Delta \mathcal{E}$. If we have n inclusions per unit volume, then the change in energy as a result of the presence of the inclusion in a volume V will be $n\Delta \mathcal{E}V$. The energy of the field in the absence of the inclusions is $\frac{1}{2}\epsilon_2 E_{i0} E_{i0} V$ where E_{i0} is the field at great distances from the particles. We may thus define an effective constant ϵ^* by the relation†

$$(5-46) \quad \frac{1}{2}\epsilon^* E_{i0} E_{i0} V = \frac{1}{2}\epsilon_2 E_{i0} E_{i0} V + n\Delta \mathcal{E}V$$

or upon rearrangement

$$(5-47) \quad \epsilon^* = \epsilon_2 + \frac{2n\Delta \mathcal{E}}{E_{i0} E_{i0}}$$

† See Eq. 5-20.

From the linearity of the Laplace equation it is easily seen that $\Delta \mathcal{E}$ must be proportional $E_{i0}E_{i0}$. Thus we may write

$$(5-48) \quad \epsilon^* = \epsilon_2(1 + n\alpha)$$

where α is a constant that depends upon ϵ_1 , ϵ_2 , and the geometry of the included particles.

5.2. Geometry of Heterogeneous Media

As we pointed out in the introduction we here consider a heterogeneous material to be a material in which the electric or elastic properties of the material vary from point to point in a manner that may best be treated from a statistical point of view. In this section we wish to discuss what is known about the geometry of such materials. In part we shall follow the discussions given in papers by Beran (1965b) and Frisch (1965). Since most attention has been paid to two-phase materials our discussion will be principally directed toward this special case.

It is clear, of course, that if we have a single sample of a material we never need consider the problem from a statistical point of view. In principal we may measure the elastic or electric constants of the sample as a function of position to any desired accuracy. The information may be stored in tabular form or perhaps in an analytic expression that is obtained by expansion in some set of complete functions. When treating heterogeneous media, however, this is usually not what we wish to do. We are almost never concerned with the detailed variation of a single sample but rather with the properties of a large class of samples that were prepared in the same overall or macroscopic manner.

For example, we may prepare a sample of a heterogeneous material by specifying the volume fractions of a number of components to be combined in a mixture, the overall manner in which they may be mixed together and some technique to insure bonding between the mixed components. The exact geometric arrangement of the mixture is left unspecified. The samples produced according to this general overall (macroscopic) prescription comprise an ensemble that forms a basis for a statistical description. Since the overall prescription was the same for all the samples they have something in common that

distinguishes this set of samples from a set produced according to a different set of overall rules.

The ensemble may be crudely characterized statistically by specifying only quantities like the mean value and standard deviation of the elastic or electric constants. In order to present a complete statistical description of the material, however, requires a knowledge of the joint probability density function

$$(5-49) \quad P_n[a(\mathbf{x}_1), a(\mathbf{x}_2), \dots, a(\mathbf{x}_n); b(\mathbf{x}_1), b(\mathbf{x}_2), \dots, b(\mathbf{x}_n); \dots;]$$

$$g(\mathbf{x}_1), g(\mathbf{x}_2), \dots, g(\mathbf{x}_n)]$$

in the limit as $n \rightarrow \infty$ where a, b, \dots, g are the elastic or electric properties which characterize the medium (see Sections 2.1.4 and 2.2.5). For example, for the elastic properties we might have $a = \mu$ (the shear modulus) and $b = \lambda$ (Lamé's constant); for the electric properties $a = \epsilon$ (the permittivity).

The function $P_n(\lim_{n \rightarrow \infty})$ contains an enormous amount of information and yields in the limit a probability density functional which gives the probability of a particular realization of the variation of the constants. It is rarely ever attainable in practice but anything short of knowledge of this functional gives only approximate statistical information about the ensemble. In practice we must usually settle for low-order correlation functions of the form

$$\frac{a(\mathbf{x}_1)a(\mathbf{x}_2)}{a(\mathbf{x}_1)a(\mathbf{x}_2)}$$

$$\frac{a(\mathbf{x}_1)b(\mathbf{x}_2)}{a(\mathbf{x}_1)b(\mathbf{x}_2)}$$

$$\frac{a(\mathbf{x}_1)a(\mathbf{x}_2)a(\mathbf{x}_3)}{a(\mathbf{x}_1)a(\mathbf{x}_2)a(\mathbf{x}_3)}$$

$$\frac{a(\mathbf{x}_1)a(\mathbf{x}_2)b(\mathbf{x}_3)}{a(\mathbf{x}_1)a(\mathbf{x}_2)b(\mathbf{x}_3)}$$

Very few measurements have been made on even these two-point and three-point moments. In fact, the only measurements with which we are familiar are currently in progress.

Theoretically the situation is not much better but we will attempt to present some information that is available. We will follow parts of the paper by Frisch (1965) and refer the reader to this paper for a more complete treatment. The heterogeneous medium that has received the most attention is the two-phase medium. This medium may be constructed, for example, by placing inclusions of one material in

Similarly

$$(5-53) \quad \gamma_2(\mathbf{r}_1, \mathbf{r}_2) \equiv \overline{E(\mathbf{r}_1)E(\mathbf{r}_2)} = \sum_{\epsilon_1=0}^1 \sum_{\epsilon_2=0}^1 P_{\epsilon_1 \epsilon_2}(\mathbf{r}_1, \mathbf{r}_2) E(\mathbf{r}_1) E(\mathbf{r}_2) \\ = P_{11}(\mathbf{r}_1, \mathbf{r}_2)$$

since again when ϵ_1 or $\epsilon_2 = 0$, correspondingly, $E(\mathbf{r}_1)$ or $E(\mathbf{r}_2) = 0$. In general we have thus

$$(5-54) \quad \gamma_n(\mathbf{r}_1, \dots, \mathbf{r}_n) \equiv \overline{E(\mathbf{r}_1) \cdots E(\mathbf{r}_n)} = P_{1 \dots 1}(\mathbf{r}_1, \dots, \mathbf{r}_n)$$

It is useful to note that the $P_{\epsilon_1 \dots \epsilon_n}$ may be expressed in general as a linear function of the $\gamma_j(r_1, \dots, r_j), j \leq n$. For example, we have the following two-point relations ($\gamma_1 = \text{constant}$)

$$(5-55) \quad P_{01}(\mathbf{r}_1, \mathbf{r}_2) = \gamma_1 - \gamma_2(\mathbf{r}_1, \mathbf{r}_2)$$

$$(5-56) \quad P_{10}(\mathbf{r}_1, \mathbf{r}_2) = \gamma_1 - \gamma_2(\mathbf{r}_1, \mathbf{r}_2)$$

$$(5-57) \quad P_{00}(\mathbf{r}_1, \mathbf{r}_2) = 1 - 2\gamma_1 + \gamma_2(\mathbf{r}_1, \mathbf{r}_2)$$

These relations may be derived using Eq. 5-51. For example, letting $k - 1 = 1$, we have

$$(5-58) \quad P_{10}(\mathbf{r}_1, \mathbf{r}_2) + P_{11}(\mathbf{r}_1, \mathbf{r}_2) = P_1(\mathbf{r}_1)$$

Since we have assumed the random media to be statistically homogeneous, all the correlation functions depend only upon relative positions rather than absolute position. Thus

$$\gamma_1(\mathbf{r}_1) = \gamma = \text{a constant}$$

$$\gamma_2(\mathbf{r}_1, \mathbf{r}_2) = \gamma_2(\mathbf{r}_{12})$$

where

$$\mathbf{r}_{12} = (\mathbf{r}_2 - \mathbf{r}_1)$$

and in general

$$\gamma_n(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = \gamma_n(\mathbf{r}_{12}, \mathbf{r}_{13}, \dots, \mathbf{r}_{1n})$$

where

$$\mathbf{r}_{1j} = \mathbf{r}_j - \mathbf{r}_1$$

Since the media have also been assumed to be isotropic

$$\gamma_2(\mathbf{r}_{12}) = \gamma_2(|\mathbf{r}_{12}|)$$

$$\gamma_3(\mathbf{r}_{12}, \mathbf{r}_{13}) = \gamma_3(|\mathbf{r}_{12}|, |\mathbf{r}_{13}|, \mathbf{r}_{12} \cdot \mathbf{r}_{13})$$

with similar simplifications for higher-order moments.

the matrix of another or by taking fine powders of two different metals, mixing them together and compressing the mixture in a mold to form a large solid sample.

The two-phase medium may be conveniently characterized by what may be termed a matter phase covering a region of space D_1 with volume fraction ϕ and a void phase covering a region of space D_0 with volume fraction $1 - \phi$. We then define a function $E(\mathbf{r})$ with the following properties:

$$E(\mathbf{r}) = 1 \quad \text{if } \mathbf{r} \in D_1 \\ = 0 \quad \text{if } \mathbf{r} \in D_0$$

For convenience theoretically, and generally as an acceptable physical hypothesis, we assume that the material is statistically homogeneous and isotropic.

It is useful to describe the two-phase materials in terms of the probability functions

$$(5-50) \quad P_{\epsilon_1 \epsilon_2 \dots \epsilon_n}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) \\ \epsilon_i = 1 \quad \text{if } \mathbf{r}_i \in D_1 \\ = 0 \quad \text{if } \mathbf{r}_i \in D_0$$

defined as the probability that at $\mathbf{r}_1, E(\mathbf{r}_1) = \epsilon_1$, and at $\mathbf{r}_2, E(\mathbf{r}_2) = \epsilon_2$, and, \dots , and at $\mathbf{r}_n, E(\mathbf{r}_n) = \epsilon_n$. For example, $P_{010}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$ is the probability that there is a matter phase at \mathbf{r}_2 and void phases at \mathbf{r}_1 and \mathbf{r}_3 . We note also that since a point must be in either D_1 or D_0 then

$$(5-51) \quad P_{\epsilon_1 \dots \epsilon_{k-1} 0}(\mathbf{r}_1, \dots, \mathbf{r}_{k-1}, \mathbf{r}_k) + P_{\epsilon_1 \dots \epsilon_{k-1} 1}(\mathbf{r}_1, \dots, \mathbf{r}_{k-1}, \mathbf{r}_k) \\ = P_{\epsilon_1 \dots \epsilon_{k-1}}(\mathbf{r}_1, \dots, \mathbf{r}_{k-1})$$

and

$$P_1(\mathbf{r}_1) + P_0(\mathbf{r}_1) = 1$$

The mean value of $E(\mathbf{r})$ may be computed from the equation

$$(5-52) \quad \gamma_1(\mathbf{r}) \equiv \overline{E(\mathbf{r})} = \sum_{\epsilon=0}^1 P_\epsilon(\mathbf{r}) E(\mathbf{r}) \\ = P_1(\mathbf{r})$$

since $E(\mathbf{r}) = 0$ when $\epsilon = 0$.

In general γ_2, γ_3 , and all higher moments are independent of each other. In the particular case when $\gamma_1 = \frac{1}{2}$ and it is impossible to distinguish the geometry of one phase from the other it is possible to determine γ_{2n+1} from γ_{2n} ; i.e., it is possible to determine the odd moment from the preceding even moment. It is not possible to determine γ_{2n+2} from γ_{2n} , these moments remain independent. The reason that this is possible results from relations like

$$P_{11\dots 1}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = P_{00\dots 0}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$$

and

$$P_{11\dots 10}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n) = P_{00\dots 01}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n)$$

We derive here the relationship between γ_3 and the γ_2 's.

Consider a sample space composed of eight events 111, 110, 101, 100, 011, 010, 001, 000 that may be interpreted, respectively, as the events: matter phase at $\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3$ (111), matter phase at $\mathbf{r}_1, \mathbf{r}_2$, void phase at \mathbf{r}_3 (110) and so on. The probability of a matter phase at $\mathbf{r}_1, P_1(\mathbf{r}_1)$, is

$$(5-59) \quad P_1(\mathbf{r}_1) = P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{110}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ + P_{101}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{100}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

Similarly, the probability of a void phase at \mathbf{r}_1 is

$$(5-60) \quad P_0(\mathbf{r}_1) = P_{011}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{010}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ + P_{001}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{000}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

The probability of a matter phase at both \mathbf{r}_1 and \mathbf{r}_2 is

$$(5-61) \quad P_{11}(\mathbf{r}_1, \mathbf{r}_2) = P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{110}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

with similar expressions for P_{10}, P_{01} , and P_{00} .

From these expressions we find the lengthy expression

$$(5-62) \quad P_1(\mathbf{r}_1) + P_1(\mathbf{r}_2) + P_1(\mathbf{r}_3) - P_{11}(\mathbf{r}_1, \mathbf{r}_2) - P_{11}(\mathbf{r}_1, \mathbf{r}_3) - P_{11}(\mathbf{r}_2, \mathbf{r}_3) \\ = P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{110}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{101}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ + P_{100}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{110}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ + P_{011}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{010}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ + P_{101}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{011}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) + P_{001}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ - P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - P_{110}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) \\ - P_{101}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - P_{011}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

which simplifies to

$$(5-63) \quad P_1(\mathbf{r}_1) + P_1(\mathbf{r}_2) + P_1(\mathbf{r}_3) - P_{11}(\mathbf{r}_1, \mathbf{r}_2) - P_{11}(\mathbf{r}_1, \mathbf{r}_3) - P_{11}(\mathbf{r}_2, \mathbf{r}_3) \\ = 1 - P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) - P_{000}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

upon noting the identity

$$P_{111} + P_{101} + P_{110} + P_{100} + P_{011} + P_{010} + P_{001} + P_{000} = 1$$

Since

$$P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = P_{000}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$$

and

$$P_1(\mathbf{r}_1) = P_1(\mathbf{r}_2) = P_1(\mathbf{r}_3) = \frac{1}{2}$$

we have

$$(5-64) \quad P_{111}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{1}{2}[P_{11}(\mathbf{r}_1, \mathbf{r}_2) + P_{11}(\mathbf{r}_1, \mathbf{r}_3) + P_{11}(\mathbf{r}_2, \mathbf{r}_3) - \frac{1}{2}]$$

or in terms of the correlation functions

$$(5-65) \quad \gamma_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \frac{1}{2}[\gamma_2(\mathbf{r}_1, \mathbf{r}_2) + \gamma_2(\mathbf{r}_1, \mathbf{r}_3) + \gamma_2(\mathbf{r}_2, \mathbf{r}_3) - \frac{1}{2}]$$

The correlation functions γ_2 and γ_3 can often be determined even for nonsymmetric media if the geometry is assumed to have some simple form. For example, we may derive the correlation functions for a material that is constructed in the following manner (see Frisch, 1965; Gilbert, 1962): points are distributed at random in a volume such that the probability of finding a point in an infinitesimal volume ΔV is proportional to ΔV and such that the position of any point is independent of the position of the other points. This may be termed a Poisson pattern and the points are called Poisson points. Next each point is made a matter point or a void point with a probability $P_1(\mathbf{r})$ or $1 - P_1(\mathbf{r})$, respectively. Since the medium is to be homogeneous, $P_1(\mathbf{r})$ is chosen to be a constant γ . An arbitrary point in space is denoted as a matter point or a void point depending upon whether or not the Poisson point closest to it is a matter or void point, respectively. An example of a two-dimensional region so defined is given in Fig. 5-5. The square points are matter Poisson points and the triangular points are void Poisson points.

In order to use this model to determine the correlation functions we must determine the probability that there is a Poisson point in a region V . Discussions of this calculation in one dimension are given

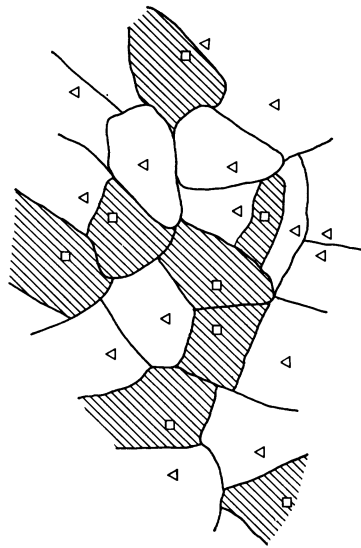


Fig. 5-5. Two-phase medium determined from a Poisson pattern.

in many texts (see, for example, Davenport and Root, 1958, or Feller, 1950). The extension to higher dimensions is immediate. Following the notation in Davenport and Root (1958), the probability $P(1, \Delta V)$ that there is one Poisson point in a small volume ΔV is

$$(5-66) \quad P(1, \Delta V) = \lambda \Delta V$$

That is, the probability is proportional to ΔV . We also have the relation

$$(5-67) \quad P(0, \Delta V) + P(1, \Delta V) = 1$$

where $P(0, \Delta V)$ is the probability that there are no Poisson points in ΔV .

Invoking the independence hypothesis

$$(5-68) \quad P(0, V + \Delta V) = P(0, V)P(0, \Delta V)$$

we then find from Eqs. 5-66, 5-67, and 5-68

$$(5-69) \quad \frac{P(0, V + \Delta V) - P(0, V)}{\Delta V} = -\lambda P(0, V)$$

and in the limit $\Delta V \rightarrow 0$

$$(5-70) \quad \frac{dP(0, V)}{dV} = -\lambda P(0, V)$$

The solution of Eq. 5-70 is

$$(5-71) \quad P(0, V) = e^{-\lambda V}$$

By similar arguments we can find the probability that there are j Poisson points in V .

We will now derive an expression for $\gamma_2(\mathbf{r}_{12})$. Similar reasoning can be used to find $\gamma_3(\mathbf{r}_{12}, \mathbf{r}_{13})$. The result will be given in terms of a quadrature as shown in the paper by Gilbert (1962). A numerical calculation is given in the paper by Frisch (1965).

Equation 5-53 allows us to interpret $\gamma_2(\mathbf{r}_{12})$ as the probability that the two points connected by the vector \mathbf{r}_{12} are both in the matter phase. Let us define $P_p(\mathbf{r}_{12})$ as the probability that the two points have the same nearest Poisson point. $\gamma_2(\mathbf{r}_{12})$ and $P_p(\mathbf{r}_{12})$ are connected by the following relation:

$$(5-72) \quad \gamma_2(\mathbf{r}_{12}) = \gamma^2(1 - P_p(\mathbf{r}_{12})) + \gamma P_p(\mathbf{r}_{12})$$

This may be seen by considering the two alternatives: (1) the two points have the same nearest Poisson point, and (2) the two points have different nearest Poisson points. The probability of statement (1) is, by the definition just given, P_p and the probability of the statement (2) is $1 - P_p$. The probability that both points are both in the matter phase is the sum of the probability that they are both in the matter phase if they have the same Poisson point and the probability that they are both in the matter phase if they do not have the same Poisson point. The probability that they are both in the matter phase if they have the same Poisson point is γP_p since by construction if one point is in the matter phase the other is also. The probability that both points are in the matter phase if they do not have the same Poisson point is $\gamma\gamma(1 - P_p)$ since the phases of the two points are not related.

The problem thus reduces to calculating $P_p(\mathbf{r}_{12})$. To do this consider the point at the origin. The probability of its nearest Poisson point being at position R, θ, ϕ, P_R , is

$$(5-73) \quad P_R = \lambda \exp[-\lambda \frac{4}{3}\pi R^3] R^2 \sin \theta \, dR \, d\theta \, d\phi$$

where θ is measured from the axis along \mathbf{r}_{12} . This follows from the fact that P_R is equal to the probability of there being no Poisson points within the sphere R multiplied by the probability that there is a Poisson point in the volume $\Delta V = R^2 \sin \theta \, dR \, d\theta \, d\phi$. This Poisson point is also the nearest Poisson point to the other point at \mathbf{r}_{12} only if there is no Poisson point in the volume $V(r, R, \theta, \phi)$ defined as the volume of a sphere of radius $r = |\mathbf{R} - \mathbf{r}_{12}|$ surrounding the point at \mathbf{r}_{12} minus the volume of the portion of space formed from the intersection of this

sphere and a sphere of radius R surrounding the point at the origin. The probability of this being true P_r is given by the expression

$$(5-74) \quad P_r = e^{-\lambda V(r, R, \theta, \phi)}$$

$P_p(r_{12})$ is then simply given as the integral over all points (R, θ, ϕ) of the product $P_r P_r$. That is,

(5-75)

$$P_p(r_{12}) = \int_0^\infty \int_0^\pi \int_0^{2\pi} \lambda \exp[-\lambda(\frac{4}{3}\pi R^3 + V(r, R, \theta, \phi))] R \sin \theta \, dR \, d\theta \, d\phi$$

This triple integral may be reduced to a double integral by a different choice of angles. (See Gilbert, 1962.) We note that $\frac{4}{3}\pi R^3 + V(r, R, \theta, \phi)$ is the union of two spheres, one centered at the origin and one centered at the point (r, θ, ϕ) .

Weissberg and Prager (1962) have derived expressions for two- and three-point correlation functions for spheres imbedded in a random manner in a matrix. The arguments they use are similar to arguments presented above and we refer the reader to this paper. Since the matter and void phases are not symmetrical in this type of medium there is no simple relation between the two- and three-point correlation function. For ease of calculation, however, they explore an approximate relation that exists between the two- and three-point correlation functions.

5.3. Definition of Effective Constants

In the introduction we discussed the definition and calculation of effective constants in a manner that we hope appealed to the reader's physical intuition. In this section we shall give a more precise definition using ensemble averages. We shall consider the definition of both electrostatic and elastic effective constants. The definition of the electrostatic constants is equivalent to the definition of effective heat conduction, electrical conduction, diffusion, or magnetostatic constants with a change of notation. In the elastic case we restrict the discussion to media that are locally isotropic. We shall consider the locally nonisotropic case, however, for the electrostatic case.

We define effective constants only for a medium that (1) may be approximated by an infinite medium that is statistically homogeneous and isotropic, and (2) is subjected to a constant average electric field on an average linear displacement field. Effective constants can be defined locally in the presence of more complex average fields but this work is currently in the research stage and much more work must be done. (See Beran, 1965c.) As we stated in the introduction, these effective constants are also intended to be appropriate when the average field varies slowly in distances that are large compared to distances over which the medium constants undergo considerable variation, or perhaps more precisely when distances are large compared to a characteristic distance for which the two-point correlation function is effectively zero. Our derivation, however, will consider only the ideal case.

In the electrostatic case we consider two vectors. We treat the electric vector $E_i(\mathbf{x})$ and the displacement vector $D_i(\mathbf{x})$. Locally we consider that they are related by the tensor relation

$$(5-76) \quad D_i(\mathbf{x}) = \epsilon_{ij}(\mathbf{x})E_j(\mathbf{x})$$

If $\epsilon_{ij}(\mathbf{x}) = \epsilon(\mathbf{x})\delta_{ij}$, the medium is locally isotropic; if the tensor contains off-diagonal terms, then the medium is locally nonisotropic. (An example of a nonisotropic heterogeneous medium would be a polycrystal wherein the permittivities along the principal axes are unequal in each crystal.) In the language of heat conductivity, for example, we would have the relation

$$(5-77) \quad q_i(\mathbf{x}) = k_{ij}(\mathbf{x})T_{,j}(\mathbf{x})$$

where $q_i(\mathbf{x})$ is the heat flux vector, $k_{ij}(\mathbf{x})$ is the heat conductivity tensor, and $T_{,j}(\mathbf{x})$ is the temperature gradient in the x_j direction.

We set as the only condition the demand that the average electric field $\overline{E_i(\mathbf{x})}$ be a constant. Since the permittivity field $\epsilon_{ij}(\mathbf{x})$ is statistically homogeneous and isotropic, no point in the medium is in any way differentiated from any other point and hence $\overline{D_i(\mathbf{x})}$ is also a constant. An expression for $\overline{D_i(\mathbf{x})}$ is obtained by averaging both sides of Eq. 5-76. We find

$$(5-78) \quad \overline{D_i(\mathbf{x})} = \overline{\epsilon_{ij}(\mathbf{x})E_j(\mathbf{x})}$$

The purpose of effective constants is to replace a basically heterogeneous material by an equivalent homogeneous material for the

purpose of discussing the behavior of average fields. Thus we seek a relation between $D_i(\mathbf{x})$ and $\epsilon_i(\mathbf{x})$ of the form

$$(5-79) \quad \overline{D_i(\mathbf{x})} = \epsilon^* \overline{E_i(\mathbf{x})}$$

where ϵ^* is termed the effective permittivity. We note that since the $\epsilon_{ij}(\mathbf{x})$ field is statistically homogeneous and isotropic, ϵ^* is a simple constant scalar function, not a tensor. The local anisotropy is averaged out. For a statistically homogeneous and isotropic permittivity field we could *not* have a relationship of the form

$$\overline{D_i(\mathbf{x})} = \epsilon_{ij}^* \overline{E_j(\mathbf{x})}$$

where the off-diagonal terms of ϵ_{ij}^* were not equal to zero. Since $\overline{E_i(\mathbf{x})}$ is in some fixed direction, for example, the $i = 3$ direction, on the basis of this information it is equally plausible for $\overline{D_i(\mathbf{x})}$ to lie in any direction in the plane perpendicular to the fixed direction. Hence, we must take $\overline{D_1(\mathbf{x})} = \overline{D_2(\mathbf{x})} = 0$.

Combining Eqs. 5-78 and 5-79 we have

$$(5-80) \quad \epsilon^* = \frac{\overline{\epsilon_{3j}(\mathbf{x})E_j(\mathbf{x})}}{E_3(\mathbf{x})} = \epsilon + \frac{\overline{\epsilon_{3j}'(\mathbf{x})E_j'(\mathbf{x})}}{E_3(\mathbf{x})}$$

where for convenience we have set the average field in the "three" directions and noted that $\epsilon_{33} = \epsilon$.

We also may deduce from the fact that

$$\overline{D_1(\mathbf{x})} = \overline{D_2(\mathbf{x})} = 0$$

the results

$$\overline{\epsilon_{ij}'(\mathbf{x})E_j'(\mathbf{x})} = \overline{\epsilon_{2j}'(\mathbf{x})E_j'(\mathbf{x})} = 0$$

In the elastic case we consider two tensors: the stress tensor $\tau_{ij}(\mathbf{x})$ and the strain tensor $\epsilon_{ij}(\mathbf{x})$. We also consider the displacement vector $u_i(\mathbf{x})$. The relationship between $\epsilon_{ij}(\mathbf{x})$ and $u_i(\mathbf{x})$ is taken to be

$$(5-81) \quad \epsilon_{ij}(\mathbf{x}) = \frac{1}{2} \left[\frac{\partial u_i(\mathbf{x})}{\partial x_j} + \frac{\partial u_j(\mathbf{x})}{\partial x_i} \right]$$

For a locally isotropic medium the relationship between $\tau_{ij}(\mathbf{x})$ and $\epsilon_{ij}(\mathbf{x})$ is

$$(5-82) \quad \tau_{ij}(\mathbf{x}) = \lambda(\mathbf{x})e_{ii}(\mathbf{x})\delta_{ij} + 2\mu(\mathbf{x})e_{ij}(\mathbf{x})$$

where $\lambda(\mathbf{x})$ is Lamé's constant and $\mu(\mathbf{x})$ is the shear modulus. $\lambda(\mathbf{x})$ and $\mu(\mathbf{x})$ are related to the bulk modulus $k(\mathbf{x})$ by the relation

$$k(\mathbf{x}) = \lambda(\mathbf{x}) + \frac{2}{3}\mu(\mathbf{x})$$

As a basic condition we require that $\overline{u_i(\mathbf{x})}$ be of the form (where α_{ij} is not identically zero)

$$(5-83) \quad \overline{u_i(\mathbf{x})} = \alpha_{ij}\overline{x_j}$$

This yields a constant average strain field

$$(5-84) \quad \overline{e_{ij}(\mathbf{x})} = \alpha_{ij}$$

Since the statistical distribution of the elastic constants is assumed to be homogeneous no point in space is to be preferred over any other point in space and $\overline{\tau_{ij}(\mathbf{x})}$ is also a constant. The expression for $\overline{\tau_{ij}(\mathbf{x})}$ is found by averaging Eq. 5-82. We have then

$$(5-85) \quad \overline{\tau_{ij}(\mathbf{x})} = \overline{\lambda(\mathbf{x})e_{ii}(\mathbf{x})\delta_{ij}} + 2\overline{\mu(\mathbf{x})e_{ij}(\mathbf{x})}$$

If we wish to replace our basic heterogeneous material by an equivalent homogeneous material that is locally isotropic, we seek a relation between $\tau_{ij}(\mathbf{x})$ and $e_{ij}(\mathbf{x})$ of the form

$$(5-86) \quad \overline{\tau_{ij}(\mathbf{x})} = \lambda^* \overline{e_{ii}(\mathbf{x})\delta_{ij}} + 2\mu^* \overline{e_{ij}(\mathbf{x})}$$

where λ^* and μ^* are effective constants that must be obtained from a comparison of Eqs. 5-85 and 5-86.

In order to see the relation between Eqs. 5-85 and 5-86 let us first write

$$\overline{\tau_{ij}(\mathbf{x})} = \overline{\tau_{ij}(\mathbf{x})} + \tau'_{ij}(\mathbf{x})$$

$$e_{ij}(\mathbf{x}) = \overline{e_{ij}(\mathbf{x})} + e'_{ij}(\mathbf{x})$$

$$\lambda(\mathbf{x}) = \overline{\lambda(\mathbf{x})} + \lambda'(\mathbf{x})$$

$$\mu(\mathbf{x}) = \overline{\mu(\mathbf{x})} + \mu'(\mathbf{x})$$

where the primed quantities have zero mean value. Introducing these expressions into Eq. 5-85 yields

$$(5-87) \quad \overline{\tau_{ij}} = [\overline{\lambda}e_{ii} + \overline{\lambda'}e'_{ii}]\delta_{ij} + 2\overline{\mu}e_{ij} + 2\overline{\mu'}e'_{ij}$$

where all the barred quantities are independent of \mathbf{x} .

Since the equations of elasticity are linear and $\overline{e_{ij}}$ is a constant tensor, we may write in general

$$(5-88) \quad \overline{e'_{ij}(\mathbf{x})} = C'_{ijmn}(\mathbf{x})\overline{e_{mn}}$$

where the $C'_{ijmn}(\mathbf{x})$ are random functions of \mathbf{x} determined by the equations of motion. Substituting Eq. 5-88 into Eq. 5-87 yields

$$(5-89) \quad \overline{\tau_{ij}} = [\overline{\lambda} \overline{e_{il}} + \overline{\lambda'} C'_{ilmn} \overline{e_{mn}}] \delta_{ij} + 2\overline{\mu} \overline{e_{ij}} + 2\overline{\mu'} C'_{ijmn} \overline{e_{mn}}$$

Eq. 5-89 may be written in the form

$$(5-90) \quad \overline{\tau_{ij}} = [\overline{\lambda} \delta_{ij} \delta_{mn} + \overline{\lambda'} C'_{ilmn} \delta_{ij} + 2\overline{\mu} \delta_{im} \delta_{jn} + 2\overline{\mu'} C'_{ijmn}] \overline{e_{mn}} \\ = C^*_{ijmn} \overline{e_{mn}}$$

Since the material properties are statistically homogeneous and isotropic and since $\overline{\tau_{ij}}$ and $\overline{e_{mn}}$ are average quantities, C^*_{ijmn} must be an isotropic tensor. Hence

$$(5-91) \quad C^*_{ijmn} = A^* \delta_{ij} \delta_{mn} + B^* \delta_{im} \delta_{jn} + C^* \delta_{in} \delta_{jm}$$

and thus we are led to Eq. 5-86:

$$(5-86) \quad \overline{\tau_{ij}} = \lambda^* \overline{e_{il}} \delta_{ij} + 2\mu^* \overline{e_{ij}}$$

where $\lambda^* = A^*$ and $2\mu^* = B^* + C^*$.

Comparing Eqs. 5-86 and Eq. 5-87, we find

$$(5-92) \quad \lambda^* = \overline{\lambda} + \frac{\overline{\lambda' e'_{il}}}{\overline{e_{il}}} \\ \mu^* = \overline{\mu} + \frac{\overline{\mu' e'_{ij}}}{\overline{e_{ij}}} \quad (\text{no summation over } i \text{ and } j)$$

if $\overline{e_{il}}$ and $\overline{e_{ij}}$ are not equal to zero.

We pointed out in Section 5.1.4 that ϵ^* , λ^* , and μ^* may also be defined by energy relations. Thus we may also write

$$(5-93) \quad \frac{1}{2} \epsilon^* \overline{E_3^2} = \overline{\frac{1}{2} \epsilon E_i E_i} = \overline{\frac{1}{2} D_i E_i} = \frac{1}{2} \overline{D_3 E_3} + \frac{1}{2} \overline{D'_i E'_i}$$

and

$$(5-94) \quad \frac{1}{2} \lambda^* \overline{e_{il} e_{ij} \delta_{ij}} + \frac{1}{2} 2\mu^* \overline{e_{ij} e_{ij}} = \frac{1}{2} \overline{\lambda e_{il} e_{ij} \delta_{ij}} + \frac{1}{2} \overline{2\mu e_{ij} e_{ij}} \\ = \frac{1}{2} \overline{\tau_{ij} e_{ij}} \\ = \frac{1}{2} \overline{\tau_{ij} e_{ij}} + \frac{1}{2} \overline{\tau'_{ij} e'_{ij}}$$

These definitions are equivalent to those given in Eq. 5-79 and Eq. 5-86, since

$$\overline{E'_i D'_i} = 0$$

and

$$\overline{e'_{ij} \tau'_{ij}} = 0$$

To show that these relations are correct, we assume an ergodic-type hypothesis and show that the volume average of these quantities approaches zero as $V \rightarrow \infty$.

For example

$$(5-95) \quad \overline{E'_i D'_i} = \frac{\partial \overline{\phi'}}{\partial x_i} D'_i = \lim_{V \rightarrow \infty} \frac{1}{V} \int \frac{\partial \phi'}{\partial x_i} D'_i dx \\ = \lim_{V \rightarrow \infty} \frac{1}{V} \int \phi' [\text{div } \mathbf{D}'] dx + \lim_{V \rightarrow \infty} \frac{1}{V} \int \nabla \cdot (\phi' \mathbf{D}') dx \\ = \lim_{V \rightarrow \infty} \frac{1}{V} \int \phi' [\mathbf{D}' \cdot \mathbf{n}] dS$$

since $\text{div } \mathbf{D}' = 0$. Assuming that the average quantity

$$\frac{1}{S} \int \phi' [\mathbf{D}' \cdot \mathbf{n}] dS$$

is bounded as $V \rightarrow \infty$, we find

$$\lim_{V \rightarrow \infty} \frac{1}{V} \int \phi' [\mathbf{D}' \cdot \mathbf{n}] dS = \lim_{V \rightarrow \infty} \frac{S}{V} \frac{1}{S} \int \phi' [\mathbf{D}' \cdot \mathbf{n}] dS = 0$$

since $(S/V) \rightarrow 0$ as $V \rightarrow \infty$. The elasticity proof proceeds similarly.

5.4. Statistical Moment Equations

In Chapter 3 we discussed the nature of a complete formulation of the statistical problem. A complete solution to the statistical problem for heterogeneous media entails a knowledge of the functional $P[E_i(\mathbf{x}), \epsilon_{im}(\mathbf{x})]$ in the electrostatic case and $P[\mu_i(\mathbf{x}), \lambda(\mathbf{x}), \mu(\mathbf{x})]$ in the

elastic case.

$$P[E_i(\mathbf{x}), \epsilon_{lm}(\mathbf{x})] dE_1(\mathbf{x}) \cdots dE_3(\mathbf{x}) d\epsilon_{11}(\mathbf{x}) \cdots d\epsilon_{33}(\mathbf{x})$$

is defined as the probability of the realization of the particular joint field $[E_i(\mathbf{x}), \epsilon_{lm}(\mathbf{x})]$. There is a similar definition for $P[\mu_i(\mathbf{x}), \lambda(\mathbf{x}), \mu(\mathbf{x})]$. Equations can be derived which govern the characteristic functional (the generalized Fourier transform of P) and in principle the solution of this equation with appropriate boundary conditions provides the complete solution to the statistical problem.

The equations governing the characteristic functionals have so far proved too difficult to solve and so approximate solutions have been sought by considering the statistical moment equations. The complete infinite hierarchy of statistical moment equations is equivalent to the equation governing the characteristic functional and is similarly intractable. To proceed we must make some assumption which reduces the infinite hierarchy of equations to a finite set with which we may cope. In the theory of heterogeneous media the only cutoff procedure that has received detailed attention is the perturbation technique. As of the writing of this book no other assumptions (as, for example, the cumulant neglect hypothesis) have been considered although there is no reason why attempts should not be made. See, however, Bourret (1962).

We shall now outline the derivation of the hierarchy of statistical moment equations for the electrostatic case with a specific form of tensor permittivity and the elastic case assuming materials with local isotropy. We shall restrict ourselves to materials that are statistically homogeneous and isotropic. We shall then apply perturbation theory to derive a set of soluble equations and conclude with a few solutions that have been obtained.

5.4.1. The Electrostatic Case

The governing equations for the electrostatic problem with tensor permittivity ϵ_{ij} are

$$(5-96) \quad \frac{\partial}{\partial x_i} D_i(\mathbf{x}) = 0$$

$$D_i(\mathbf{x}) = \epsilon_{ij}(\mathbf{x}) E_j(\mathbf{x})$$

$$(5-97) \quad \delta_{ijk} \frac{\partial}{\partial x_j} E_k(\mathbf{x}) = 0$$

In the following development of the statistical moment equations we shall follow the procedure presented by Molyneux (1964).

$\epsilon_{ij}(\mathbf{x})$ is a symmetric tensor. We denote the values of $\epsilon_{ij}(\mathbf{x})$ along the principal axes at \mathbf{x} , by $\epsilon_{(i)}(\mathbf{x})$; $(i) = 1, 2, 3$. In terms of the principal axes we write $\tilde{\epsilon}_{ij}(\mathbf{x}) = \epsilon_{(i)}(\mathbf{x}) \delta_{ij}$; (i) indicates no summation on i . The unit vectors along the fixed-reference axis are denoted by n_i and the unit vectors along the local principal axes are denoted by $\nu_i(\mathbf{x})$. The principal axes at a point are specified by the tensor functions $a_{ij}(\mathbf{x})$ which in turn are defined as

$$(5-98) \quad a_{ij}(\mathbf{x}) = \nu_i(\mathbf{x}) \cdot n_j$$

$$\text{where } a_{ij} a_{ik} = a_{ji} a_{ki} = \delta_{jk}$$

$\epsilon_{ij}(\mathbf{x})$ and $\tilde{\epsilon}_{ij}(\mathbf{x})$ are related by the expression

$$(5-99) \quad \begin{aligned} \epsilon_{ij}(\mathbf{x}) &= a_{ki}(\mathbf{x}) a_{mj}(\mathbf{x}) \tilde{\epsilon}_{km}(\mathbf{x}) \\ &= a_{ki}(\mathbf{x}) a_{kj}(\mathbf{x}) \epsilon_{(k)}(\mathbf{x}) \end{aligned}$$

We have distinguished $a_{ij}(\mathbf{x})$ and $\epsilon_{(k)}(\mathbf{x})$ since they both may vary. In the subsequent development we shall, for simplicity, consider the special case in which $\epsilon_{(k)}(\mathbf{x})$ is independent of \mathbf{x} . When $\epsilon_{(k)}(\mathbf{x})$ is independent of \mathbf{x} , the average value of $\epsilon_{ij}(\mathbf{x})$ is given by

$$(5-100) \quad \overline{\epsilon_{ij}} = \overline{a_{ki}(\mathbf{x}) a_{kj}(\mathbf{x})} \epsilon_{(k)}$$

Since we assume that the media are statistically homogeneous and isotropic, $a_{ki}(\mathbf{x}) a_{kj}(\mathbf{x}) \epsilon_{(k)}$ must be independent of \mathbf{x} and proportional to δ_{ij} . It may be shown that

$$(5-101) \quad \overline{a_{(k)i}(\mathbf{x}) a_{(k)j}(\mathbf{x})} = \frac{1}{3} \delta_{ij}$$

Thus we have

$$(5-102) \quad \begin{aligned} \overline{\epsilon_{ij}} &= \frac{1}{3} (\epsilon_1 + \epsilon_2 + \epsilon_3) \delta_{ij} \\ &= \bar{\epsilon} \delta_{ij} \end{aligned}$$

We shall later need an expression for $\overline{\epsilon_{ij} \epsilon_{kl}}$. Direct calculation shows

$$(5-103) \quad \begin{aligned} \overline{\epsilon_{ij} \epsilon_{kl}} &= \frac{1}{15} (\epsilon_1^2 + \epsilon_2^2 + \epsilon_3^2) [\delta_{ij} \delta_{kl} + \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}] \\ &\quad + 2(\epsilon_1 \epsilon_2 + \epsilon_1 \epsilon_3 + \epsilon_2 \epsilon_3) \left[\frac{2}{15} \delta_{ij} \delta_{kl} - \frac{1}{30} (\delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk}) \right] \end{aligned}$$

For convenience we now write the permittivity tensor in the form

$$(5-104) \quad \epsilon_{ij}(\mathbf{x}) = \overline{\epsilon_{ij}} + \epsilon'_{ij}(\mathbf{x}) = \bar{\epsilon} \delta_{ij} + \epsilon'_{ij}(\mathbf{x})$$

where $\bar{\epsilon} = \frac{1}{3}(\epsilon_1 + \epsilon_2 + \epsilon_3)$. We also write the principal values $\epsilon_{(i)}$ in the form

$$(5-105) \quad \epsilon_{(i)} = \bar{\epsilon} + \Delta\epsilon_{(i)}$$

We then find

$$(5-106) \quad \epsilon'_{ij}(\mathbf{x}) = a_{ki}(\mathbf{x})a_{kj}(\mathbf{x})\Delta\epsilon_{(k)} - \frac{1}{3}(\Delta\epsilon_1 + \Delta\epsilon_2 + \Delta\epsilon_3)\delta_{ij}$$

In the perturbation analysis we shall have most need for the two-point correlation function

$$C_{ijk\ell}(\mathbf{x}_1, \mathbf{x}_2) = \overline{\epsilon'_{ij}(\mathbf{x}_1)\epsilon'_{kl}(\mathbf{x}_2)}$$

In terms of the functions $a_{ij}(\mathbf{x})$ we find

$$(5-107) \quad C_{ijk\ell}(\mathbf{x}_1, \mathbf{x}_2) = \overline{a_{pi}(\mathbf{x}_1)a_{pj}(\mathbf{x}_1)a_{qk}(\mathbf{x}_2)a_{q\ell}(\mathbf{x}_2)} \\ \cdot \Delta\epsilon_{(p)}\Delta\epsilon_{(q)} - \frac{1}{3}(\Delta\theta_1)^2\delta_{ij}\delta_{kl}$$

where $\Delta\theta_1 = \Delta\epsilon_1 + \Delta\epsilon_2 + \Delta\epsilon_3$.

When $\mathbf{x}_1 = \mathbf{x}_2$, the function reduces to

$$(5-108) \quad C_{ijk\ell}(\mathbf{x}_1, \mathbf{x}_1) = -\frac{2}{45}(\Delta\theta_1)^2 - 3\Delta\theta_2)\delta_{ij}\delta_{kl} \\ + \frac{2}{45}(\Delta\theta_1)^2 - 3\Delta\theta_2)[\delta_{ij}\delta_{jk} + \delta_{ik}\delta_{jl}]$$

where

$$\Delta\theta_2 \equiv \Delta\epsilon_1\Delta\epsilon_2 + \Delta\epsilon_1\Delta\epsilon_3 + \Delta\epsilon_2\Delta\epsilon_3$$

The function $C_{ijk\ell}(\mathbf{x}_1, \mathbf{x}_2)$ is assumed to be homogeneous and thus we have

$$(5-109) \quad C_{ijk\ell}(\mathbf{x}_1, \mathbf{x}_2) = C_{ijk\ell}(\mathbf{r})$$

where $\mathbf{r} = \mathbf{x}_2 - \mathbf{x}_1$.

Furthermore, since the tensor $\epsilon'_{ij}(\mathbf{x})$ is symmetric then $C_{ijk\ell}(\mathbf{r})$ has the following properties

$$(5-110) \quad C_{ijk\ell}(\mathbf{r}) = C_{jik\ell}(\mathbf{r}) = C_{ijlk}(\mathbf{r}) = C_{klij}(-\mathbf{r})$$

Since $C_{ijk\ell}(\mathbf{r})$ is an isotropic tensor it has the form (see Batchelor, 1953)

$$(5-111) \quad C_{ijk\ell}(\mathbf{r}) = P(r)r_i r_j r_k r_\ell + Q(r)r_i r_j \delta_{kl} + R(r)r_j r_k \delta_{li} \\ + Q'(r)r_k r_\ell \delta_{ij} + R'(r)r_i r_j \delta_{jk} + R''(r)r_i r_k \delta_{jl} \\ + R'''(r)r_j r_\ell \delta_{ik} + S(r)\delta_{ij}\delta_{kl} + T(r)\delta_{ik}\delta_{jl} \\ + T'(r)\delta_{il}\delta_{jk}$$

where the functions $P(r)$, $Q(r)$, $Q'(r)$, $R(r)$, \dots are even scalar functions of r . (Primes do not denote derivatives here.)

The conditions given in Eq. 5-110 demand that

$$(5-112) \quad Q(r) = Q'(r)$$

$$R(r) = R'(r) = R''(r) = R'''(r)$$

$$T(r) = T'(r)$$

When $\epsilon_{(i)}(\mathbf{x})$ is independent of \mathbf{x} , as we take it to be here, then $\epsilon'_{ii} = 0$ and we have the condition

$$(5-113) \quad C_{iik\ell}(\mathbf{r}) = C_{ij\ell i}(\mathbf{r}) = 0$$

In this case we have the additional restraints

$$(5-114) \quad r^2 P + 3Q + 4R = 0$$

$$(5-115) \quad r^2 Q + 3S + 2T = 0$$

In general we have five independent scalars characterizing the two-point correlation tensor $C_{ijk\ell}(\mathbf{r})$. When $\epsilon_{(i)}(\mathbf{x})$ is independent of \mathbf{x} we need only three independent scalar functions to characterize $C_{ijk\ell}(\mathbf{r})$. Similar analyses may be made for the higher-order correlation tensors but the algebra is very involved and to this writer's knowledge no one has as yet taken on the task of analyzing the character of these functions.

We now write the basic equations 5-96 and 5-97 in terms of average and fluctuating components. We write $\epsilon_{ij}(\mathbf{x})$ in the form given by Eq. 5-104 and write for $E_i(\mathbf{x})$

$$(5-116) \quad E_i(\mathbf{x}) = \overline{E_i(\mathbf{x})} + E'_i(\mathbf{x})$$

This yields for the basic equations

$$(5-117)$$

$$\bar{\epsilon} \frac{\partial \overline{E_i(\mathbf{x})}}{\partial x_i} + \bar{\epsilon} \frac{\partial E'_i(\mathbf{x})}{\partial x_i} + \frac{\partial}{\partial x_i} \epsilon'_{ij}(\mathbf{x}) \overline{E_j(\mathbf{x})} + \frac{\partial}{\partial x_i} \epsilon'_{ij}(\mathbf{x}) E'_j(\mathbf{x}) = 0$$

$$(5-118) \quad \delta_{ijk} \frac{\partial \overline{E_k(\mathbf{x})}}{\partial x_j} + \delta_{ijk} \frac{\partial E'_k(\mathbf{x})}{\partial x_j} = 0$$

In order to determine a hierarchy of moment equations we write Eqs. 5-117 and 5-118 explicitly in terms of the independent variable \mathbf{x}_1 .