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Linear response of two-phase composites with cross moduli: Exact universal relations

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We consider the linear-response properties of composites made of two isotropic materials. We concentrate on linear-response phenomena, with nonvanishing cross coefficients, such as the magnetoelectric effect, the thermoelectric effect, and coupled, multispecies diffusion. We find that the moduli of the composite must obey a number of compatibility relations, involving the moduli of the components, but totally independent of the mixture ratio of the components and the microstructure of the composite. The compatibility conditions take the form $C(L,L_a,L_b)\equiv LL_a^{-1}L_b-L_bL_a^{-1}L=0$, where L_a,L_b are the response matrices of the components, and L is that of the composite. These come about because there exists a choice of driving forces and fluxes—an eigenbasis—that are decoupled in both components. When the composite itself is isotropic, these constitute $n(n-1)/2$ relations that its moduli must obey (for real response matrices), leaving only n independent coefficients to be specified—n being the number of driving fields. When the composite is anisotropic, the elements of L are spatial tensors and the same conditions apply as relations between these tensors. In the latter case one can eliminate the moduli of the components, and obtain relations that the moduli of the composite must satisfy among themselves. The mere fact that the composite is made of two isotropic components, without any further information, imposes strong relations among its moduli. For example, we show that all the tensor moduli of such a composite are symmetric. The same compatibility conditions must also be obeyed by the response matrices of any three composites of the same two isotropic components; so, knowledge of the moduli of two composites supplies constraints on any third, or, for that matter, on the components themselves. We discuss the general properties of the compatibility conditions and their possible relation to parallel and series construction of composites, and demonstrate our findings for the most common case of two driving fields in three dimensions. The compatibility conditions apply not only for the effective response matrices of well-homogenized composites, but also for the local response—at any point within some region that is filled with an arbitrary two-phase mixture—to the potentials on the boundary of the region. All the above apply, with little change, to the case where the response matrices are complex-symmetric or Hermitian. We have nothing to add to the lore on composites, in the case where all the cross coefficients vanish; the compatibility conditions are identities in this case. All our results remain intact for multiphase composites, when all the components but two are either perfect conductors or perfect insulators.

I. INTRODUCTION

There exists an enormous lore on the effective linear moduli of composites that are made of two components—or phases.[1,2] Most of the present knowledge pertains to systems with uncoupled linear-response properties. Particularly noteworthy are the results on bounds of various sorts on the allowed values of the effective constants of two-phase mixtures.[3–9]

In contrast, we shall concern ourselves, in this paper, with the moduli of multifield, *coupled,* or cross linear-response, in which the application of one driving force induces not only its own conjugate flux but also other fluxes. Two distinct types of phenomena are involved: Equilibrium phenomena, which are exemplified by the magnetoelectric effect,[10] whereby the application of either a magnetic field or an electric field induces an electric polarization as well as a magnetization. The other class includes dissipative, nonequilibrium phenomena such as the thermoelectric effect,[11] in which thermal and electric transports are coupled; similarly, one finds that, often, the diffusion of particles of different species through some materials or membranes is coupled, involving so-called cross effects.[12] A partial treatment of the thermoelectric effect in composites can be found in Ref. 13.

We will show that in such materials, with nonvanishing cross moduli, the allowed values of the effective moduli of any composite are strongly constrained not only by the known bounds, but, in fact, by exact compatibility relations that they must satisfy. Moreover, these relations are oblivious to the volume fractions of the components and the microstructure of the composite. Given only the moduli of the components, those of the composite must obey a large number of universal linear relations among themselves.

Consider a linear-response problem, in a space of arbitrary dimension d involving n driving fields, derivable from potentials $\phi=(\phi_1,\phi_2,\ldots,\phi_n)$, and the vector of fluxes $\mathbf{F}=(\mathbf{F}_1,\mathbf{F}_2,\ldots,\mathbf{F}_n)$. When the material is isotropic the fluxes are related to the driving fields in the linear approximation, that we assume all along, by

$$\mathbf{F}=-L\nabla\phi\ , \tag{1}$$

where L is the $n\times n$ response matrix.

The system possesses a generating function G in which the elements of L appear as parameters. In the equilibrium case G is some energy function (such as the free energy) that is a functional of the degrees of freedom ϕ of the problem. By virtue of the structure of G, L is a symmetric matrix. The functional G attains a minimum in the equilibrium state and for this to be stable, L must be positive definite. The Euler-Lagrange equations derived from G are

$$\nabla\cdot\mathbf{F}=\nabla\cdot(L\nabla\phi)=0\ . \tag{2}$$

For a dissipative phenomenon the role of the generating function is played by the entropy-increase rate.[14] One can work, in this case also, with *divergenceless fluxes.* The elements of L are the kinetic coefficients, and the Onsager reciprocity relations[14] state that the matrix L is symmetric, in general. One exception occurs when one of the intensive parameters on which L depends, in general, is an externally applied magnetic field H in which case $L_{km}(H)=L_{mk}(-H)$. We take all along $H=0$. Casimir[15] pointed out another exception: When some of the potentials are even under time reversal, say the first k of them, and the rest are odd, then elements of L connecting fields with different time-parity are antisymmetric. Then, L takes the form

$$L=\begin{bmatrix} S^{(1)} & B \\ -\tilde{B} & S^{(2)}\end{bmatrix}\ , \tag{3}$$

with $S^{(i)}$ symmetric. We are not aware of a continuous system for which this needs be taken into consideration, and assume thus that the response matrices we deal with are symmetric; exceptions will then receive a special treatment.

As the entropy-generation function is positive, L must be positive in the dissipative case as well. The symmetry and positive definiteness of L, which are compelled by different physical arguments in the two types of phenomena, will play a crucial role in our derivation of the compatibility conditions.

We derive the compatibility conditions in Sec. II and expound their properties in Sec. III. In Sec. IV, we generalize to the case of anisotropic composites. Section V concerns composite, electric circuits. In Sec. VI, we demonstrate our results for the case of two fields. Section VII summarizes our findings and discusses further issues.

II. DERIVATION OF THE COMPATIBILITY RELATIONS

Consider two *isotropic* substances, a and b, with their response matrices L_a,L_b, respectively. Within each substance separately, the fluxes and potentials are related by

$$\mathbf{F}=-L_s\nabla\phi,\quad s=a,b\ ; \tag{4}$$

the L's are real, symmetric, and positive-definite (the nonreal case will be discussed below).

Given two such matrices, one can diagonalize them *simultaneously* by a congruent transformation, using a real, regular matrix W, such that

$$\begin{aligned} WL_a\tilde{W}&=\lambda^a=\mathrm{diag}(\lambda_1^a,\lambda_2^a,\ldots,\lambda_n^a)\ ;\\ WL_b\tilde{W}&=\lambda^b=\mathrm{diag}(\lambda_1^b,\lambda_2^b,\ldots,\lambda_n^b)\ . \end{aligned} \tag{5}$$

(The matrix W is not orthogonal, in general; indeed it cannot be if L_a,L_b do not commute.)

To prove this, one first diagonalizes, say, L_a by a *similarity* transformation U; then one rescales the fields such that L_a is transformed into the unit matrix (this can be done only when L_a is positive definite); the combined transformation takes L_b into another symmetric matrix which can, in turn, be diagonalized by another similarity transformation; the latter does not affect L_a any further (as it is the unit matrix now). The desired matrix W is the product of these three transformations.[16]

Now, define the eigenpotentials and eigenfluxes as

$$\psi=\tilde{W}^{-1}\phi,\quad \mathbf{J}=W\mathbf{F}\ . \tag{6}$$

In terms of these fields, the response matrices in the two substances are given by λ^a and λ^b . Also, $\sum_k \mathbf{J}_k\cdot\nabla\psi_k=\sum_k \mathbf{F}_k\cdot\nabla\phi_k$; so, the generating function is invariant under (6). Now, in the eigenbasis of the problem, every flux-potential pair is decoupled from all the others in each of the substances. In component a one has $\mathbf{J}_k=\lambda_k^a\nabla\psi_k$, while in b, $\mathbf{J}_k=\lambda_k^b\nabla\psi_k$. Moreover, the eigenfluxes satisfy $\nabla\cdot\mathbf{J}_k=0$, because they are linear combinations-with coefficients that are fixed for the problem—of the physical fluxes $\mathbf{F}$. Hence, in any composite of a and b, an applied $\nabla\psi_k$ for any k can drive only the flux $\mathbf{J}_k$. In other words, the response matrix of any composite cannot connect different eigenpotentials of the problem.

We treat, first, isotropic composites, and defer the treatment of anisotropic composites to Sec. IV. In the former case, the effective response matrix of the composite is also an $n\times n$ matrix L. As we have just shown, it must also be diagonal in the eigenbasis,

$$WL\tilde{W}=\lambda=\mathrm{diag}(\lambda_1,\lambda_2,\ldots,\lambda_n)\ . \tag{7}$$

It is clear at this point that L is given, once one specifies the n values of the elements of λ; the relations between L and λ are through W, which depends only on L_a,L_b. All the information on the volume fractions of the components and the microstructure of the composite enters through the constants λ_i. Thus, the $n(n+1)/2$ measurable elements of L—which are quite arbitrary for a general medium—must satisfy $n(n-1)/2$ constraints that depend only on the elements of L_a,L_b. We now proceed to derive these constraints.

Obviously, λ, λ^a, and λ^b all commute. This fact can be cast in forms that involve only L, L_a, and L_b but not W. For example, writing

$$\lambda(\lambda^a)^{-1}\lambda^b-\lambda^b(\lambda^a)^{-1}\lambda=0\ , \tag{8}$$

we get

$$C(L,L_a,L_b) \equiv LL_a^{-1}L_b - L_bL_a^{-1}L = 0 \; . \tag{9}$$

These are the desired compatibility conditions.

One can also write more relations such as $[\lambda^{-1}\lambda^a,\lambda^{-1}\lambda^b]=0$ leading to $[L^{-1}L_a,L^{-1}L_b]=0$ and other such relations; they can all be shown to add nothing to Eq. (9).

The same arguments apply for the response matrices of *any three composites made of the same two components.* These matrices must commute in the eigenbasis and hence in the physical basis they must satisfy the compatibility conditions. Hence, it is enough to measure the response matrices of two composites to provide constraints on any third (including any of the two components).

We now attend to cases where the response matrices are not real symmetric as we assumed in the proof. When the problem can be formulated in terms of complex potentials and fluxes with Hermitian, positive-definite response matrices, the same proof applies, *mutatis mutandis,* and Eq. (9) must still be satisfied.

Many linear-response problems of interest are described by complex, symmetric response matrices. Strictly speaking, our proof fails in this case because not all complex, symmetric matrices can be diagonalized by a matrix U satisfying $\tilde{U}=U^{-1}$ (U may now be complex). However, the set of $n\times n$ complex, symmetric matrices that cannot be diagonalized in this way is a set of measure zero among all the complex, symmetric matrices. For example, for $n=2$, only the four-real-parameter family of matrices of the form

$$Z=\begin{bmatrix} 2z_1 & \pm i(z_1-z_2) \\ \pm i(z_1-z_2) & 2z_2 \end{bmatrix} , \tag{10}$$

with z_1,z_2 arbitrary, complex numbers, cannot be diagonalized, out of the six real-parameter set of all complex, symmetric matrices. (These are the matrices with two equal eigenvalues.) Barring such unlikely occurrences for the response matrices, the compatibility condition must apply here as well. In the complex case, where the response matrices may depend on the frequency of the driving fields, the compatibility conditions must hold for every frequency.

III. GENERAL PROPERTIES OF THE COMPATIBILITY RELATIONS

The compatibility conditions enjoy some very useful symmetries and superposition properties. These can be straightforwardly derived *from the compatibility conditions themselves*—without reference to the way in which the latter where arrived at—and we state them here without detailing the proofs.

(1) As expected, the conditions $C(L,L_a,L_b)=0$ are symmetric in L_a and L_b. In fact, they are totally symmetric with respect to the three arguments of C. Knowledge of any two of the three constrains the third.

(2) The conditions are satisfied automatically for the cases $L=L_a$ and $L=L_b$.

(3) When the three arguments are diagonal, the compatibility conditions are identities, so we have nothing to add to the knowledge of such systems.

(4) If two matrices commute, and the third is compatible with them, the latter must also commute with them.

(5) If three matrices are compatible, so are their inverses.

(6) If matrices $L_1,L_2,\dots,$ are compatible with L_a and L_b, so is any linear or harmonic combination of them; i.e., any matrix of the forms $\sum_i \nu_i L_i$, or $(\sum_i \nu_i L_i^{-1})^{-1}$ (ν_i are numbers). Thus, the series or parallel combination of mixtures that are compatible with two components, produces another one that is also compatible with them.

Given two of the matrix arguments of the compatibility function, the compatibility conditions constitute linear equations in the components of the third. How many independent equations do we get thus? When the response matrices are symmetric (Hermitian), as we have assumed so far, the compatibility matrix C is antisymmetric (anti-Hermitian). One then has $n(n-1)/2$ real conditions in the real case, and $n(n-1)$ real conditions in the complex-symmetric case, and in the Hermitian case.

When the arguments of C have the Casimir form [Eq. (3)], then C can be shown to take the form

$$C=\begin{bmatrix} A^{(1)} & B \\ \tilde{B} & A^{(2)} \end{bmatrix} , \tag{11}$$

where $A^{(i)}$ are antisymmetric matrices. Again we see that only one set of $n(n-1)/2$ off-diagonal elements of C are independent.

Are all these conditions linearly independent? We conjecture without proof that in the generic case, where no degeneracies are present, they are. We checked this by algebraic computation technics for the case $n=3$ (and trivially for $n=2$) and found that, indeed, in the general case, the three compatibility equations obtained are independent: any three of the six unknowns determine the other three.

IV. ANISOTROPIC COMPOSITES

Many composites, even of isotropic components, are themselves anisotropic. Such are, for instance, laminated structures, or composites in which one component is in the form of aligned, similar, triclinic grains, or in the form of long needles or fibers–as in fiber reinforced materials. For arbitrary anisotropic materials exhibiting a coupled linear-response phenomenon in d space dimensions, the relations between potentials and fluxes are

$$F_{k\alpha} = -\sum_{m\beta} L_{km\alpha\beta}\partial_\beta\phi_m \; . \tag{12}$$

Latin indices designate the field type, as before; Greek indices designate space coordinates: $\alpha,\beta=1,\dots d$. The response matrix is symmetric with respect to the simultaneous exchange of both: $L_{km\alpha\beta}=L_{mk\beta\alpha}$. For a fixed pair of fields, ϕ_k,ϕ_m, let $T(km)$ be the $d\times d$ matrix whose $\alpha\beta$ element is $L_{km\alpha\beta}$, it is the space-tensor modulus of the material (such as the heat-diffusion tensor, the dielectric tensor, the thermoelectric tensor, etc.). The Ts are, in general, asymmetric tensors, unless $k=m$, in which case the symmetry of L dictates that they are. We can write L as an $nd \times nd$ matrix of the form

$$L = \begin{bmatrix} T(11) & T(12) & \cdots & T(1n) \\ \tilde{T}(12) & T(22) & \cdots & T(2n) \\ \vdots & \vdots & \ddots & \vdots \\ \tilde{T}(1n) & \tilde{T}(2n) & \cdots & T(nn) \end{bmatrix} . \tag{13}$$

As we argued in Sec. II, in the eigenbasis of the problem, L must be diagonal in the field indices; i.e., the response matrix of a composite of two *isotropic* materials, in this basis, takes the form

$$\lambda_{km\alpha\beta} = t^k_{\alpha\beta}\delta_{km} . \tag{14}$$

For fixed α and β we get a matrix that is diagonal in km. This implies—as all our basis changes do not act on the space indices—that for every $\alpha\beta$, L, as a matrix in km, must satisfy the compatibility conditions [Eq. (9)]. We thus get d^2 such matrix conditions. In other words, if in Eq. (9) we put for the km-matrix-element of L, the space-tensor matrix $T(km)$, we get the generalization the compatibility conditions for anisotropic composites.

Interestingly enough, we can now extract from the compatibility conditions, relations between the moduli of the composite with no information on those of the components. The mere fact that the composite is made of *two isotropic* components constrains its allowed response matrix.

For example, in the general case, where no special degeneracies are present, every tensor coefficient $T(km)$ can be written—through the compatibility conditions—as a linear combination of the n tensors $T(ii)$, lying along the diagonal of L. The latter are, however, all symmetric, and so must all the $T(km)$'s be. This can also be deduced from the fact that the $T(km)$ are linear combinations of the symmetric tensors t^k appearing in Eq. (14). To recapitulate: all the tensor moduli of an anisotropic composite of two isotropic materials are symmetric (this is not the case for an arbitrary material).

There are additional constraints that make no use of the moduli of the components. These come about in the following way: the response matrix of a general anisotropic materials has $nd(nd+1)/2$ independent components (we confine our discussion here to the real case, the generalization to the complex case is straightforward). The compatibility conditions provide $d^2n(n-1)/2$ constraints on those, with parameters that depend on the moduli of the components. [These are, in general, independent; as we can see from Eq. (14), only $nd(d+1)/2$ constants need be specified, to determine all the elements of L of the composite; thus, there must exist $d^2n(n-1)/2$ independent compatibility conditions.] The number of these parameters is smaller than the number of constraint; so, they can be eliminated, leaving some constraints that involve the moduli of the composite only. The above symmetry requirements account for some of these constraints, but some still remain.

A different, and more useful, way of perceiving the existence of such component-independent relations is as follows: The d^2, $n \times n$ matrices $l(\alpha\beta)$ formed from L by fixing the space indices, are diagonal in the eigenbasis, and hence, every three of them must satisfy the compatibility conditions among themselves, just as any three composite response matrices must. In such relations, the moduli of the components do not appear, and we are left with the desired relations

$$C[l(\alpha\beta), l(\gamma\delta), l(\epsilon\eta)] = 0 , \tag{15}$$

for all the choices of the six space indices (not all of these relations are independent).

We note here that, in general, the principal axes of the different tensor coefficients, $T(km)$, need not be the same. In composites that have symmetry axes—such as laminar ones—all $T(km)$ do commute and can be diagonalized in the same axes. In this frame we have d matrices $l(\alpha\alpha)$; $\alpha=1,\ldots d$. On these, we have $\binom{d}{3}$ sets of compatibility conditions—each set still consisting of $n(n-1)/2$ conditions. In three-dimensional composites with common principal axes, there is at least one such set of component-independent conditions—always in addition to the conditions that relate the composite to the components.

We shall demonstrate all this for the case $d=3, n=2$ in Sec. VI.

V. ELECTRICAL CIRCUITS AS DISCRETE REALIZATIONS

We now discuss electrical circuits as examples of discrete systems that are subject to the compatibility conditions. One need not bring the above proof to bear on circuits; the necessity of the compatibility conditions follows directly from their general properties and the construction of the circuits.

Consider electrical circuits (that we shall term n-pair circuits) having n pairs of external terminals: $1,1';2,2';\ldots n,n'$ (n will be fixed for the rest of our discussion), with an internal structure that guarantees that the current I_i going into terminal i is the same as that coming out of i'. Let V_i be the voltage difference between i' and i. Suppose we describe the system by the impedance matrix Z such that the voltage vector $V=(V_1,V_2,\ldots,V_n)$ is given by $V=ZI$, where $I=(I_1,I_2,\ldots,I_n)$ is the vector of currents. V, I, and Z may be complex, and Z frequency dependent.

If any number of n-pair circuits with impedances $Z_a, Z_b, \ldots$, are connected in series (terminal i' of each to terminal i of the next), we get another n-pair circuit whose impedance matrix Z is the sum of Z_m. We call this an additive connection with respect to Z. When circuits are connected in parallel the inverses of Z_m add to give the inverse of Z and we term this a harmonic connection with respect to Z.

Now, consider two n-pair circuits, a and b, with Z_a and Z_b, respectively, which we use as basic building blocks, to build any n-pair circuit following these rules: Beginning with a number of a and b circuits, we build the circuit in stages; in each stage we put together, into an n-

pair circuit, either in series or in parallel, any number of n-pair circuits built by the same rules in previous stages. It is clear that the impedance matrix of the resulting circuit must satisfy the compatibility conditions with Z_a, Z_b; so, for that matter, must the impedance matrices of any three circuits composed in this way (from the same building blocks a and b). This follows, straightforwardly, by induction, from properties (2) and (6) of the compatibility conditions (Sec. III) and we need not resort to the proof given for the continuous case.

When the circuits contain only standard elements, the Onsager theorem applies, and the impedance matrix must be symmetric. The circuit may, however, contain gyrators: time-reversal antisymmetric elements.[17] The matrix Z is then not symmetric but has the Casimir form. The compatability conditions must still apply for composite n-pair circuits containing gyrators (because the additive and harmonic joining of the response matrix still applies).

The n-pair circuits themselves offer more examples of such systems with asymmetric response matrices: Pick any k of the n terminal pairs—say the first k—and call them even, while the rest we call odd. Instead of working with the impedance matrix, describe the system by the matrix N that gives $V^* \equiv (V_1, V_2, \ldots V_k, I_{k+1}, \ldots I_n)$ in terms of $I^* \equiv (I_1, I_2, \ldots, I_k, V_{k+1}, \ldots, V_n)$: $V^* = NI^*$. It is straightforward to show that, if Z is symmetric,

$$Z = \begin{bmatrix} R & Q \\ \tilde{Q} & S \end{bmatrix} , \tag{16}$$

with R and S (complex) symmetric of orders k and $n-k$, respectively (and S^{-1} exists) then, N has the form of a response matrix in the Casimir case [Eq. (3)]

$$N = \begin{bmatrix} R - QS^{-1}\tilde{Q} & QS^{-1} \\ -S^{-1}\tilde{Q} & S^{-1} \end{bmatrix} . \tag{17}$$

One can define connections of n-pair circuits that are additive and harmonic with respect to the N matrices. Here, in the additive connection, even terminals are connected in series, while odd ones are connected in parallel. In this way, the V^* vector for the combined circuit is the sum of those of the components, while the I^* vectors of all the components and of the composite are all equal. In the harmonic connection, the even terminals are connected in parallel and the odd ones in series. As before, all circuits hierarchically constructed from two basic units, must have N matrices that obey the compatibility conditions.

These results for circuits—for which the necessity of the compatibility conditions is quite evident—are interesting for themselves, but they may also illuminate the applicability of these conditions to continuous cases. It may well be that the appearance of a microstructure-independent and mixing-fraction-independent compatibility conditions is a vestige of a parallel and series combination of the two component substances to form the composite. This view may be strengthened by noting that all the moduli of an isotropic composite can be determined by cutting a thin slice of the composite, making each of its two faces an equipotential, and measuring the fluxes which will be perpendicular to the surface. In this one-dimensional configuration, it is easier to envisage the composite as being put together by a successive series and parallel joining of pieces.

What can we learn from circuits about continuous systems with Casimir-type response matrix? Does the fact that circuits of this type conform to the compatibility conditions imply that continuous systems do too? This need not be the case; the topology of wiring circuits allows one to interchange the role of any number of driving potentials and their conjugate fluxes. This can always be used to achieve an equivalent description of the system by a *symmetric* response matrix. We know then that the most general composite circuit is specified by only n-independent moduli. It is not surprising then that the compatibility conditions apply. In the continuous, isotropic case, all fluxes flow in the same channels, so to speak, and we cannot think of a physically meaningful description whereby some fluxes are swapped with driving forces, in a way analogous to connecting some wires in parallel instead of in series.

The validity of the compatibility conditions for the Casimir case remains an open question for us.

VI. EXAMPLES

We shall now look in some detail into the case of most immediate interest: two driving fields in three dimensions. For concreteness we shall describe the universal results in the context of the magnetoelectric effect, whereby each of the two isotropic components is described by its dielectric constant and permeability: ϵ_i and μ_i, respectively, and by the magnetoelectric coefficient α_i ($i = 1,2$ for material 1 and 2, respectively).

There is here only one compatibility relation for the effective coefficients ϵ, μ, α, of an isotropic composite. In this $n=2$ case, the condition can be conveniently written as

$$\begin{vmatrix} \epsilon & \mu & \alpha \\ \epsilon_1 & \mu_1 & \alpha_1 \\ \epsilon_2 & \mu_2 & \alpha_2 \end{vmatrix} = 0 , \tag{18}$$

exhibiting the symmetry of the condition in the three materials. The three triads of coefficients are in one plane in the ϵ, μ, α space.

The two-field result also serves as an approximation when all the off-diagonal elements of the response matrices involved are small compared with the diagonal ones, and may be taken only to first order. In this case, the compatibility conditions break into $n(n-1)/2$ two-field compatibility conditions, one for each pair of fields.

In the degenerate case where one of the three minors multiplying one of the effective coefficients vanishes, e.g., $\epsilon_1\mu_2 - \epsilon_2\mu_1 = 0$, the condition gives a relation between the other two.

We have calculated the three effective coefficients of an isotropic composite by solving directly the field equations, with the appropriate boundary conditions, for the coated sphere composite.[3] In this composite, space is filled with spheres of different sizes, each made of a sphere of one material coated with a spherical shell of the other, with a fixed ratio of radii. The problem was solved exactly with the aid of computer-algebraic technics. The effective constants are rather cumbersome functions of the volume-ratio of the two components and of their constants. It was then verified that they satisfy Eq. (18).

We now turn to the anisotropic case. The effective moduli ϵ,μ,α are now 3×3 tensors that, satisfy Eq. (18). Because ϵ and μ must be symmetric, Eq. (18) implies that α is also a symmetric space tensor—barring the degeneracy $\epsilon_1/\epsilon_2=\mu_1/\mu_2$. Thus, an anisotropic composite of two isotropic magnetoelectric materials cannot have a vector (antisymmetric) magnetoelectric effect. This may be due to the fact that one cannot define a vector in such a mixture.

An orthorombic magnetoelectric material has, in general, nine independent constants, three for each modulus. An orthorombic composite of two isotropic material has, as we now show, only eight. There are three compatibility conditions that relate those nine to the coefficients of the components. As we stated for the general case, the latter can be eliminated to give relations between the effective constants, that require no knowledge of the components (except that they are isotropic). In our case, one such relation remains, and it can be obtained, directly, by noting that the three matrices

$$\begin{bmatrix}\epsilon_{xx} & \alpha_{xx}\\ \alpha_{xx} & \mu_{xx}\end{bmatrix},\quad \begin{bmatrix}\epsilon_{yy} & \alpha_{yy}\\ \alpha_{yy} & \mu_{yy}\end{bmatrix},\quad \begin{bmatrix}\epsilon_{zz} & \alpha_{zz}\\ \alpha_{zz} & \mu_{zz}\end{bmatrix}, \tag{19}$$

must obey the compatibility condition, Eq. (18), which reads here as

$$\begin{vmatrix}\epsilon_{xx} & \mu_{xx} & \alpha_{xx}\\ \epsilon_{yy} & \mu_{yy} & \alpha_{yy}\\ \epsilon_{zz} & \mu_{zz} & \alpha_{zz}\end{vmatrix}=0\ . \tag{20}$$

A general (triclinic), anisotropic material has 21 independent constants describing a two-field phenomenon: in our case, six each for the dielectric and permeability tensors, and nine for the magnetoelectric tensor. Our analysis shows that an anisotropic composite of two isotropic materials has only 14 independent constants. Three of the 21 fall because the cross modulus must be symmetric, thus using three of the total of nine compatibility conditions—one for each pair of space indices. Of the remaining six, two can be used to eliminate the two parameters that depend on the constants of the components entering the compatibility conditions. The remaining four relations can be cast in a determinant form similar to Eq. (20): In addition to Eq. (20) we now write three equations with zz in the last row replaced by xy, xz, and yz. These four conditions amount to stating that the six triads $\epsilon_{\gamma\delta},\mu_{\gamma\delta},\alpha_{\gamma\delta}$ are in the same plane in the ϵ,μ,α plane $(\gamma,\delta=x,y,z)$. (The 14 independent constants must still obey two conditions relating them to the moduli of the components.) These are special cases of Eq. (15).

When the response matrix of one component (say 2) is a multiple of the unit matrix—which is the case, for example, for the effective constants of a porous magnetoelectric material (one component being vacuum)—the compatibility conditions for the tensor moduli reduce to

$$\alpha=\frac{\alpha_1}{(\epsilon_1-\mu_1)}(\epsilon-\mu)\ . \tag{21}$$

Thus—as the constants of the components enter through only one parameter, $\alpha_1/(\epsilon_1-\mu_1)$, that needs be eliminated—there are only 13 independent constants (seven in the orthorombic case).

We calculated—by solving the Maxwell equations—the dielectric, permeability, and magnetoelectric tensor moduli for two porous media, both involving triaxial ellipsoids surrounded by vacuum. The first was the coated-ellipsoid configuration in which space is filled with similar, oriented, triaxial ellipsoids—with an assortment of sizes—each made of an inner ellipsoid of an isotropic material, surrounded by vacuum inside a larger ellipsoid confocal with the inner one; here the composite has an orthorombic symmetry (the principal axes of the three moduli are the same). The other configuration is a diluted mixture of (noninteracting) triaxial ellipsoids in vacuum, with different axes ratios and different orientations; here the three moduli may have different principal axes. As expected, we find that Eq. (21) is satisfied in both cases.

VII. CONCLUSIONS AND DISCUSSION

We have shown that the allowed linear-response moduli of composites made of two isotropic components are strongly constrained by a set of compatibility conditions in the form of algebraic equations containing only the moduli of the components and of the composite. The volume fractions of the components do not appear, nor do the details of the microstructure. The same relations are obeyed by the moduli of any three composites of the same two components, and require no knowledge of the moduli of the latter. All the response matrices of composites of the same two isotropic materials have to be of the form $W^{-1}\lambda\tilde{W}^{-1}$, where λ is diagonal with elements that are positive (and conform to the known bounds on the moduli of uncoupled response matrices). For anisotropic composites of isotropic components, relations exist between the effective constants, that are altogether independent of the moduli of the components.

All through the paper we have treated the composite as homogeneous on the scale over which the gradients of the potentials are obtained from differences and over which the fluxes are averaged. In fact, however, the compatibility conditions apply under more general circumstances for a system that is not necessarily homogenized. Consider a region, R, of space, with a boundary Σ. On Σ one dictates the potentials as boundary conditions of the form

$$\phi_m(\sigma)=\phi_{m0}b(\sigma);\quad \sigma\in\Sigma\ , \tag{22}$$

where, $b(\sigma)$ is the same for all potentials and ϕ_{m0} are constants. (The treatment is generalized straightforwardly to the Neumann boundary conditions.) The region is filled with some material and one measures the fluxes at

$\mathbf{r}\in R$; linearity implies that the α space component of the fluxes is given by

$$F_k^\alpha(\mathbf{r}) = -\Lambda_{km}^\alpha(\mathbf{r})\phi_{m0} ; \tag{23}$$

$\Lambda^\alpha(\mathbf{r})$ may be considered the response matrix, at $\mathbf{r}$, to the potentials on Σ; it depends on the choice of R, on $b(\sigma)$, as well as on the distribution of L in R. When R is filled with a homogeneous, isotropic medium with a response matrix L, it is easy to see that

$$\Lambda_{km}^\alpha(\mathbf{r}) = L_{km}\partial_\alpha g(\mathbf{r}) , \tag{24}$$

where $g(\mathbf{r})$ is the solution of the Laplace equation in R, with $b(\sigma)$ as boundary condition. If we now fill R with two isotropic components in whatever fashion—possibly with pieces not much smaller than R itself—we find, using arguments as in Sec. II, that any three matrices $\Lambda^\alpha(\mathbf{r})$, each corresponding to an arbitrary choice of α, $\mathbf{r}$, R, or $b(\sigma)$, but with the filling material being a mixture of the same two components, must satisfy the compatibility conditions among themselves. Our findings for the effective response matrices of composites are all special cases of this result. Also, we see that to check our findings, experimentally, one needs not prepare a homogenized composite; for example, one can work with an arbitrary mixture filling the space between two parallel condenser plates that are each an equipotential.

Our interest here has been focused on relations that are independent of details of the preparation of the composite. We can, however, make the following note concerning bounds: There are various constraints known for uncoupled phenomena in the form of bounds on the (uncoupled) moduli of the composites in terms of those of the components.[4,5] We can now put these to use by bounding the diagonal elements of L in the eigenbasis (λ_i) in terms of λ_i^a and λ_i^b. These bounds can, in turn, be formulated as bounds on the elements of L that depend on those of L_a, L_b. We hope to demonstrate this procedure and describe the resulting bounds in a future publication.

Many results that are known to hold for the single-field case are straightforwardly generalized to the coupled multifield case using the following procedure. Take any such result constituting an equality or an inequality involving the constants of the components and of the mixture. If this result holds for all the eigenfields, it can be written as a diagonal-matrix relation. This relation has then to be written such as to have, on each side, an expression of the form $\ldots\lambda^a(\lambda^b)^{-1}\lambda^c(\lambda^d)^{-1}\ldots$, where the λ's are the diagonal response matrices in the eigenbasis, all of which transform in the same way. The same relation then holds in the physical basis, with the λ's replaced by the L's. We give a few examples of this procedure in Ref. 18 deriving, among other things, the effective response matrix for the coated-sphere model. Here we give, as another example, the generalization of the relation[19,20] between the principal effective constants $\epsilon_x^*, \epsilon_y^*$ of a two-dimensional, two-phase mixture of isotropic components having constants ϵ_1 and ϵ_2

$$\epsilon_x^*(\epsilon_1,\epsilon_2)\epsilon_y^*(\epsilon_2,\epsilon_1) = \epsilon_1\epsilon_2 . \tag{25}$$

In the multifield case this relation holds for any of the elements of the (diagonal) response matrices in the eigenbasis. We then write for these matrices

$$\lambda_x^*(\lambda_1,\lambda_2)\lambda_1^{-1}\lambda_y^*(\lambda_2,\lambda_1)\lambda_2^{-1} = I , \tag{26}$$

where I is the unit matrix; this generalizes to

$$L_x^*(L_1,L_2)L_1^{-1}L_y^*(L_2,L_1)L_2^{-1} = I , \tag{27}$$

as we can see by multiplying Eq. (26) by W on the left and W^{-1} on the right, and inserting the appropriate factors of $\tilde{W}\tilde{W}^{-1}$, etc., in between the factors. (We thank K. Schulgasser for suggesting that we generalize this relation.)

We now list some of the limitations that, we think, our analysis is subject to. We have not been able to extend the results to composites of more than two components. It is, in general, impossible to diagonalize simultaneously three symmetric matrices in the way that underlies our derivation for two components. For a composite that is made of three components by preparing first a composite of two of them which is then mixed with the third, our analysis shows that it is enough to specify $2n$ constants for the final composite to determine all the rest (when all the samples involved are isotropic, say). But this helps only if $n > 3$, and besides, such a composite is, of course, not the general three-component composite. A likewise unlikely three-phase composite is one in which the response matrix of a component is a linear combination of the other two. All matrices can then be diagonalized simultaneously, and the compatibility conditions still apply. Similar arguments apply to composites with more components.

There is, however, an important class of multiphase mixtures that is still amenable to our treatment: all the components *but two* are either perfect "conductors" or perfect "insulators." In the former case, all the potentials are constant within a conductor; in the latter, all the fluxes vanish within an insulator. An example for the former is a superconductor in the thermoelectric case or vacuum in the case of particle diffusion; the latter case is exemplified by vacuum in the thermoelectric case (neglecting radiation transport). The presence of the added components could render the effective properties of the composite, trivial—i.e., if the conductor percolates in the direction along which the fluxes are measured; we assume that this is not the case. The effect of the presence of the added phases is purely geometrical. The mixture may be considered a two-phase one, but with appropriate boundary conditions on the contact areas of the normal phases with the added components: Constant potentials in the case of a conductor and a vanishing normal component of all the fluxes, for an insulator. At any rate, the eigenfields—defined as before, with regard to the two normal components—remain decoupled, and all our previous results remain intact.

In the same context, we ask what is the appropriate compatibility conditions, when we have only one normal phase which is neither a perfect conductor nor an insulator? Examples are the thermoelectric effect or multispecies diffusion in a porous medium. Again, the effect is purely geometrical and the compatibility conditions amount to saying that the response matrix of the composite must commute with that of the normal component; this matrix relation consists, as before, of $n(n-1)/2$ relations among the coefficients.

Our method is also limited in that the changes of bases that we employ must operate on the potentials and not on the driving forces themselves as we must preserve the fact that the fields are derivable from potentials. Also, diagonalizing the response matrices in the space coordinates will prove futile, as the field equations couple the coordinates. Thus, the Hall effect, and the thermomagnetic effect, are not directly amenable to our treatment. We also have not found a way to generalize our results to the general case of nonscalar potentials—such as effects involving elastic stresses—because here there is more than one way to couple the fields derived from the same potential, even in isotropic materials. Again, the need to diagonalize more than two matrices, simultaneously, would arise. In some special cases of this type where every two potentials interact through only one coupling, our results do apply for the matrices of coupling coefficients. Other exceptions are, for example, the piezoelectric and piezomagnetic effects in two-dimensional composites (i.e., a cylindrical configuration) when the strains are limited to axial shears, and the components have a cubic symmetry.

We have also been limited to isotropic components. It is evident that, be this not the case, we would have effectively had to diagonalize more than two matrices simultaneously (even if a composite is prepared such that the principal axes in all the regions of a given component are all aligned).

Milgrom and Shtrikman[21] have used arguments, similar to those employed in this paper, to derive constraints on the response matrices of polycrystals that are made of a single uniaxial crystal. The two symmetric matrices that define the eigenbasis, in that case, are the two principal response matrices of the uniaxial single crystal.

There are various approximations that are used to calculate effective moduli of composites (for example, the coherent potential approximation[22]). For some approximations, the response matrices calculated consistently also satisfy the compatibility conditions.

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