Theory of Disordered Systems

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Lecture 3: The Hashin-Shtrikman Bounds

In what follows we formulate a much finer variational principle for heat production and obtain stronger bounds on the conductance of a disordered system (again, as an example, in a two-phase setup). Using simple test functions we then obtain the optimal bounds for a conductivity of such a system, and discuss then the accuracy of our previous approximations, like EMA. The ideas of this chapter again rely on the existence of two conjugated fields, a potential and a solenoidal one, defining the total energy, the energy production or a similar property. The original work (Z. Hashin, S. Shtrikman, J. Appl. Phys. **33**, 3125 (1962)) considered magnetic permeability of a composite material. The discussion below follows the original work (with some additional explanations and corrections of misprints), but concentrate on a conductance of a composite material to use the same notation as in the previous lecture. The results can be generalized to more complex situations like lattice problems, and to elastic problems. We do not discuss such situations here to keep the discussion as simple as possible (it is not quite simple anyhow!).

1 The variational principle

We now formulate the stronger variational principle for heat production in a disordered system with conductance

$$\sigma(x) = \sigma_0 + \delta\sigma(x)$$

where σ_0 will be considered (at the beginning) as an arbitrary constant (not necessarily the "mean" conductance).

We introduce the two auxiliary quantities

$$\mathbf{E}' = \mathbf{E} - \mathbf{E_0}$$

and

$$\mathbf{T} = \mathbf{j} - \sigma_0\mathbf{E} = \delta\sigma(x)\mathbf{E}$$

and show that

$$U_T = \int_\Omega \left(\sigma_0 E_0^2 - \frac{T^2}{\sigma - \sigma_0} + 2\mathbf{T}\mathbf{E}_0 + \mathbf{T}\mathbf{E}' \right) dV$$

is stationary under boundary condition

$$\mathbf{E}'|_{\partial\Omega} = 0$$

and additional condition

$$\mathrm{div}\mathbf{j} = 0 \qquad \text{i.e.} \qquad \sigma_0 \, \mathrm{div}\mathbf{E}' + \mathrm{div}\mathbf{T} = 0$$

when

$$\mathbf{T} = (\sigma - \sigma_0)\mathbf{E}. \tag{1}$$

In this case the stationary value of U_T is equal to the Joule heat

$$U_{T,stat} = \int_\Omega \mathbf{j}\mathbf{E} dV.$$

Moreover

$$U_T = \max \quad \text{if } \sigma_0 < \sigma(x) \tag{2}$$

$$U_T = \min \quad \text{if } \sigma_0 > \sigma(x). \tag{3}$$

Since the mean conductance is given by

$$\sigma^* = \frac{Q}{VE_0^2}$$

we can use U_T with different test functions $\mathbf{T}$ to obtain the bounds for Q and thus for σ^*.

To see that if $\mathbf{E}$ is the actual field, $U_T = Q$ we substitute Eq.(1) into the expression for U_T which assumes the form

$$U_T = \int_\Omega \left[\sigma_0 (\mathbf{E_0})^2 - (\sigma - \sigma_0)\mathbf{E}^2 + 2(\sigma - \sigma_0)\mathbf{E}\mathbf{E_0} + (\sigma - \sigma_0)\mathbf{E}\mathbf{E}' \right] dV.$$

We now transform the integrand as follows:

$$\begin{aligned} & \sigma_0 (\mathbf{E_0})^2 - (\sigma - \sigma_0)\mathbf{E}^2 + 2(\sigma - \sigma_0)\mathbf{E}\mathbf{E_0} + (\sigma - \sigma_0)\mathbf{E}\mathbf{E}' \\ = \; & \sigma_0 (\mathbf{E_0})^2 - (\sigma - \sigma_0)\mathbf{E}^2 + (\sigma - \sigma_0)\mathbf{E}\mathbf{E_0} + (\sigma - \sigma_0)\mathbf{E}^2 \\ = \; & \sigma_0 (\mathbf{E_0})^2 + (\sigma - \sigma_0)\mathbf{E}\mathbf{E_0}. \end{aligned}$$

We now note that

$$\int_\Omega \sigma_0(\mathbf{E_0})^2 dV = \int_\Omega \sigma_0 \mathbf{E_0}(\mathbf{E_0}+\mathbf{E}')dV = \int_\Omega \sigma_0 \mathbf{E}\mathbf{E_0} dV$$

since

$$\int_\Omega \mathbf{E}' dV = 0$$

because $\mathbf{E_0} = V^{-1}\int_\Omega \mathbf{E}dV$. Now we get

$$U_T = \int_\Omega \sigma \mathbf{E}\mathbf{E_0} dV = \int_\Omega \sigma \mathbf{E}^2 dV = Q.$$

To check this it is enough to write $\mathbf{E_0} = -\mathrm{div}\,\phi_0$ and note that $\mathrm{div}\,\mathbf{j} = \mathrm{div}\,(\sigma\mathbf{E}) = 0$ so that

$$U_T = -\int_\Omega \sigma\mathbf{E}\nabla\phi_0 dV = -\int_\Omega \nabla(\sigma\mathbf{E}\phi_0)dV = -\int_{\partial\Omega} \mathbf{j}\phi_0 d\mathbf{s} = -\int_{\partial\Omega} \mathbf{j}\phi d\mathbf{s} = IU$$

(with U being the potential difference between the plates) since the potential $\phi_0 = \phi$ at the two sides of the system where the potential is applied, and $\mathbf{j} = 0$ everywhere at the rest of the system's boundary (outside of the area filled by the conductive medium).

Now the variational principle itself has to be proved.

2 The proof

Let us consider the variation of U_T under small variation of $\mathbf{E}'$. Since our functional is essentially a quadratic form of $\mathbf{E}'$ ($\mathbf{T}$ and $\mathbf{E}'$ are connected via linear relation), the variation of U_T is restricted to the second order:

$$\Delta U_T = \delta U_T + \delta^2 U_T.$$

2.1 First order

In the first order we get:

$$\delta U_T = \int_\Omega \left[2\left(-\frac{T}{\sigma-\sigma_0} + \mathbf{E}_0 + \mathbf{E}' \right)\delta\mathbf{T} - \delta\mathbf{T}\mathbf{E}' + \mathbf{T}\delta\mathbf{E}' \right] dV \tag{4}$$

The terms in the round brackets add up to zero under the assumption that $\mathbf{T} = (\sigma - \sigma_0)\mathbf{E} = (\sigma - \sigma_0)(\mathbf{E}_0 + \mathbf{E}')$. It stays to show that

$$\delta U_T = \int_\Omega \left[-\delta \mathbf{T}\mathbf{E}' + \mathbf{T}\delta\mathbf{E}'\right] dV \qquad (5)$$

vanishes.

This property follows from the additional condition $\operatorname{div} \mathbf{j} = 0$ i.e.

$$\sigma_0 \operatorname{div} \mathbf{E}' + \operatorname{div} \mathbf{T} = 0 \qquad (6)$$

from which it follows that

$$\sigma_0 \mathbf{E}' + \mathbf{T} = \mathbf{C} \qquad (7)$$

where $\mathbf{C}$ is a solenoidal vector field,

$$\operatorname{div} \mathbf{C} = 0.$$

Note that $\delta\mathbf{C}$ also has to be solenoidal, $\operatorname{div} \delta\mathbf{C} = 0$.

Inserting Eq.(7) into Eq.(5) we get

$$\delta U_T = \int_\Omega \left(-\delta \mathbf{C}\mathbf{E}' + \mathbf{C}\delta\mathbf{E}'\right) dV = -\int_\Omega \left(\delta \mathbf{C}\mathbf{E}'\right) dV + \int_\Omega \left(\mathbf{C}\delta\mathbf{E}'\right) dV. \qquad (8)$$

Now a simple mathematical trick follows. Let us introduce the potential deviation ψ' so that

$$\mathbf{E}' = -\nabla\psi'$$

and note that according to the fact that $\mathbf{E}'|_{\partial\Omega} = 0$ we have $\psi'|_{\partial\Omega} = const$ (and this constant can be set to zero) and $\delta\psi'|_{\partial\Omega} = 0$. Now we note that

$$\int_\Omega \left(\mathbf{C}\delta\mathbf{E}'\right) dV = -\int_\Omega \left(\mathbf{C}\nabla\delta\psi'\right) dV = -\int_\Omega \nabla\left(\mathbf{C}\delta\psi'\right) dV$$

and, along the same lines,

$$\int_\Omega \left(\delta\mathbf{C}\mathbf{E}'\right) dV = -\int_\Omega \nabla\left(\delta\mathbf{C}\psi'\right) dV.$$

Now we transform both volume integrals into the ones over the boundary of the system:

$$\int_\Omega \left(\mathbf{C}\delta\mathbf{E}'\right) dV = \int_{\partial\Omega} \mathbf{C}\delta\psi' d\mathbf{s}$$

and

$$\int_\Omega \left(\delta\mathbf{C}\mathbf{E}'\right) dV = \int_{\partial\Omega} \delta\mathbf{C}\psi' d\mathbf{s}$$

and note that both vanish due to the fact that $\psi'|_{\partial\Omega} = \delta\psi'|_{\partial\Omega} = 0$. Applying these results to Eq.(8) we see that $\delta U_T = 0$.

2.2 Second order

To check to whether the stationary value corresponds to a minimum or to a maximum of the corresponding functional it is necessary to consider its second order variation. In this order we have

$$\delta^2 U_T = \int_\Omega \left(-\frac{(\delta \mathbf{T})^2}{\sigma - \sigma_0} + \delta \mathbf{T} \delta \mathbf{E}' \right) dV.$$

To obtain the inequalities (2) and (3) we rewrite this expression using Eq.(7) and expressing $\delta\mathrm{T}$ via $\delta\mathrm{E}'$.

Thus, $\delta\mathrm{T} = \delta\mathrm{C} - \sigma_0 \delta\mathrm{E}'$ so that

$$\begin{aligned} \delta^2 U_T &= \int_\Omega \left(-\frac{(\delta \mathbf{C} - \sigma_0 \delta \mathbf{E}')^2}{\sigma - \sigma_0} + (\delta\mathrm{C} - \sigma_0 \delta \mathbf{E}')\delta \mathbf{E}' \right) dV \\ &= \int_\Omega \left[-\frac{1}{\sigma - \sigma_0} (\delta \mathbf{C})^2 - \left(\frac{\sigma_0^2}{\sigma - \sigma_0} + \sigma_0 \right) (\delta \mathbf{E}')^2 \right] dV \\ &\quad + \left(2\frac{\sigma_0}{\sigma - \sigma_0} + 1 \right) \int_\Omega \delta \mathbf{C} \delta \mathbf{E}' dV \end{aligned}$$

The last integral vanishes, since $\delta \mathbf{E}' = -\nabla \delta \psi'$ and $\nabla \delta \mathbf{C} = 0$ so that

$$\begin{aligned} \int_\Omega (\delta \mathbf{C} \delta \mathbf{E}')\, dV &= -\int_\Omega (\delta \mathbf{C} \nabla \delta \psi')\, dV = -\int_\Omega \nabla (\delta \mathbf{C} \delta \psi')\, dV \\ &= -\int_{\partial\Omega} \delta \mathbf{C} \delta \psi' d\mathbf{s} = 0 \end{aligned}$$

because the variation of ψ' on the boundary is zero. The first integral is however definitely negative for $\sigma > \sigma_0$. Thus the inequality (2) is proved.

For $\sigma < \sigma_0$ we first note that due to the same reason

$$\int_\Omega (\delta \mathbf{T})^2 dV = \int_\Omega (\delta \mathbf{C} - \sigma_0 \delta \mathbf{E}')^2 dV = \int_\Omega (\delta \mathbf{C})^2 dV - \sigma_0^2 \int_\Omega (\delta \mathbf{E}')^2 dV$$

(since the integral of the cross-term vanishes as shown above) and use this expression to eliminate $\delta \mathbf{E}'$ from the previous result. We obtain

$$\begin{aligned} \delta^2 U_T &= \int_\Omega \left(-\frac{(\delta \mathbf{C} - \sigma_0 \delta \mathbf{E}')^2}{\sigma - \sigma_0} + (\delta\mathrm{C} - \sigma_0 \delta \mathbf{E}')\delta \mathbf{E}' \right) dV \\ &= \int_\Omega \left[\frac{1}{\sigma_0} (\delta \mathbf{C})^2 - \frac{\sigma \sigma_0}{\sigma - \sigma_0} (\delta \mathbf{T})^2 \right] dV \end{aligned}$$

which is definitely positive for $\sigma < \sigma_0$. This finishes the proof of this remarkable relation.

3 A homogeneous and isotropic system

Taking $\mathbf{T} = const$ in each of the phase (with jumps at each phase boundary), i.e. $\mathbf{T} = \mathbf{T}_i$ in phase i, we get:

$$\frac{U_T}{V} = \sum_{i=1}^{m} \left(\sigma_0 E_0^2 - \frac{T_i^2}{\sigma_i - \sigma_0} + 2\mathbf{T_i E_0} \right) v_i + \frac{1}{V} \int_{\Omega} \mathbf{TE}' dV.$$

where m is the number of different phases, and v_i is the portion of the total volume occupied by the phase i, $\sum_i v_i = 1$. The last (integral) term, in which both $\mathbf{T}$ *and* $\mathbf{E}'$ depend on i has to be transformed in a more handy form. We now perform this transformation to show that this term $U' = V^{-1} \int_{\Omega} \mathbf{TE}' dV = \langle T^2 \rangle - \langle \mathbf{T} \rangle^2$. To do so we pass to the Fourier representation.

Let us consider the system in form of a large cube with side L and write

$$\mathbf{T}(\mathbf{r}) = \langle \mathbf{T} \rangle + \sum_{\mathbf{k} \neq 0} \mathbf{T_k} \exp\left(2\pi i \mathbf{kr}\right).$$

where $\mathbf{k} = \mathbf{n}/L$ defines the wave number ($\mathbf{n}$ is here a *triple* of whole numbers) and $\langle \mathbf{T} \rangle$ is the zeroth Fourier component. We note that since $\mathbf{T}(\mathbf{r})$ is real $\mathbf{T_k} = \mathbf{T_{-k}}$. We note that according to Eq.(6)

$$-\sigma_0 \Delta \psi' + \nabla \mathbf{T} = 0,$$

i.e.

$$\sigma_0 k^2 \psi'_{\mathbf{k}} + i\mathbf{kT_k} = 0,$$

so that

$$\psi'_{\mathbf{k}} = \frac{1}{i\sigma_0} \frac{\mathbf{kT_k}}{k^2}.$$

Returning to $\mathbf{E}'$ we can put down

$$U' = -\frac{1}{\sigma_0} \sum_{\mathbf{k} \neq 0} \left(\mathbf{kT_k}\right) \left(\mathbf{kT_k}\right)^* \frac{1}{k^2}.$$

For $L \to \infty$ we can pass from the sum to the integral over $\mathbf{k}$. We moreover assume that the integral converges quite rapidly to neglect the role of the boundaries.

Now, the most important point comes! If the system is macroscopically homogeneous and isotropic, all properties depend only on the absolute value of k and not on its direction: $\mathbf{T_k} = \mathbf{T}_k$. Therefore the corresponding integral can be rewritten as

$$
\begin{aligned}
U' &= -\frac{1}{\sigma_0}\sum_{\mathbf{k}\neq 0}\frac{1}{k^2}\left(\mathbf{k}\mathbf{T}_k\right)\left(\mathbf{k}\mathbf{T}_k\right)^* \\
&= -\frac{2\pi}{\sigma_0}\int\frac{1}{k^2}\left[\left(|\mathrm{Re}(\mathbf{T}_k)||k|\cos\theta + i|\mathrm{Im}(\mathbf{T}_k)||k|\cos\theta\right)\times\right. \\
&\quad \left.\times\left(|\mathrm{Re}(\mathbf{T}_k)|k|\cos\theta - i|\mathrm{Im}(\mathbf{T}_k)|k|\cos\theta\right)\right] d\cos\theta k^2 dk \\
&= -\frac{4\pi}{3\sigma_0}\int \mathbf{T}_k\mathbf{T}_k^* k^2 dk
\end{aligned}
\tag{9}
$$

Now we can use the relation

$$
\langle T^2\rangle = \frac{1}{V}\int_\Omega T^2 dV = \sum_{\mathbf{k}}\mathbf{T_k}\mathbf{T_k^*} = \langle T\rangle^2 + \sum_{\mathbf{k}\neq 0}\mathbf{T_k}\mathbf{T_k^*} = \langle T\rangle^2 + 4\pi\int\mathbf{T}_k\mathbf{T}_k^* k^2 dk
$$

(Parceval's identity) to rewrite the whole expression as

$$
\frac{U_T}{V} = \sum_{i=1}^{m}\left(\sigma_0 E_0^2 - \frac{T_i^2}{\sigma_i - \sigma_0} + 2\mathbf{T_i}\mathbf{E_0}\right)v_i - \frac{1}{3\sigma_0}\left[\sum_i T_i^2 v_i - \left(\sum_i \mathbf{T_i}v_i\right)^2\right]
\tag{10}
$$

and look for the stationarity condition by writing $\mathbf{T_i} = (T_{x,i}, T_{y,i}, T_{z,i})$, $\mathbf{E_0} = (E_{x,0}, E_{y,0}, E_{z,0})$, differentiating the corresponding expression with respect to $T_{\alpha,i}$ and setting the corresponding derivatives to zero. One obtains then

$$
-\frac{2}{\sigma_i - \sigma_0}T_{\alpha,i}v_i + 2E_{\alpha_0}v_i - \frac{2}{3\sigma_0}T_{\alpha,i}v_i - \frac{2}{3\sigma_0}v_i\left(\sum_i \mathbf{T_i}v_i\right) = 0
$$

i.e.

$$
\mathbf{T}_i = \frac{\mathbf{E_0} + \left(\sum_i \mathbf{T_i}v_i\right)/3\sigma_0}{(\sigma_i - \sigma_0)^{-1} + (3\sigma_0)^{-1}} = \frac{\mathbf{E_0} + \langle\mathbf{T}\rangle/3\sigma_0}{(\sigma_i - \sigma_0)^{-1} + (3\sigma_0)^{-1}}.
$$

Now we multiply both parts of these expressions for different i by v_i and sum them up to obtain

$$
\langle\mathbf{T}\rangle = \sum_i \frac{\mathbf{E_0} + \langle\mathbf{T}\rangle/3\sigma_0}{(\sigma_i - \sigma_0)^{-1} + (3\sigma_0)^{-1}}v_i.
$$

We solve this equation for $\langle\mathbf{T}\rangle$,

$$
\langle\mathbf{T}\rangle = \frac{A}{1 - A/3\sigma_0}\mathbf{E_0}
$$

with

$$A = \sum_i \frac{v_i}{(\sigma_i - \sigma_0)^{-1} + (3\sigma_0)^{-1}}$$

and substitute the full expression into Eq.(10). Using the fact that

$$\sigma^* = \frac{1}{E_0^2} \frac{U_{T,stat}}{V}$$

and the corresponding inequalities (2) and (3) we get that

$$\sigma^* > \sigma_0 + \frac{A}{1 - A/3\sigma_0} \qquad \text{for} \qquad \sigma_0 < \sigma_i, \qquad i = 1, ..., m$$

and

$$\sigma^* < \sigma_0 + \frac{A}{1 - A/3\sigma_0} \qquad \text{for} \qquad \sigma_0 > \sigma_i, \qquad i = 1, ..., m.$$

4 Application to a two-phase system

Now we explicitely consider the two-phase situation $m = 2$ with $\sigma_1 < \sigma_2$ and set $v_1 = p$ and $v_2 = 1 - p$. Taking $\sigma_0 = 0$ and $\sigma_0 \to \infty$ we obtain the pair of constraints

$$p\sigma_1 + (1-p)\sigma_2 \leq \sigma^* \leq \left(\frac{p}{\sigma_1} + \frac{1-p}{\sigma_2} \right)^{-1} \tag{11}$$

reproducing the bounds of parallel/sequential layers known from Lecture 1. The borders are quite weak, and they are realized in anisotropic situations, i.e. are not optimal for the isotropic case. Now let is consider the bounds generated by $\sigma_0 = \sigma_1 - \epsilon$ and $\sigma_0 = \sigma_2 + \epsilon$ with positive $\epsilon \to 0$. Now the following bounds are obtained:

$$\sigma_1 + \frac{1-p}{1/(\sigma_2 - \sigma_1) + p/3\sigma_1} \leq \sigma^* \leq \sigma_2 + \frac{p}{1/(\sigma_1 - \sigma_2) + (1-p)/3\sigma_2}.$$

Since the only place the dimension of space enters our discussion is the evaluation of the integral, Eq.(9), the last result can be easily generalized to a whatever space dimension d and the final relation reads

$$\sigma_1 + \frac{1-p}{1/(\sigma_2 - \sigma_1) + p/d\sigma_1} \leq \sigma^* \leq \sigma_2 + \frac{p}{1/(\sigma_1 - \sigma_2) + (1-p)/d\sigma_2}. \tag{12}$$

For weak to medium contrast the bounds Eq.(12) are quite close to each other (much closer than the ones given by Eq.(11)), see Homework 2.

Hashin and Shtrikman have shown that the borders are indeed optimal, i.e. can be realized in a system which is homogeneous and isotropic on the average by an Apollonian package of two phase balls, as shown in Fig.1. The system shown in the right panel is not "disordered" in the everyday sense, but the order is really extremely complex! For the discussion I strongly recommend to read the original work!

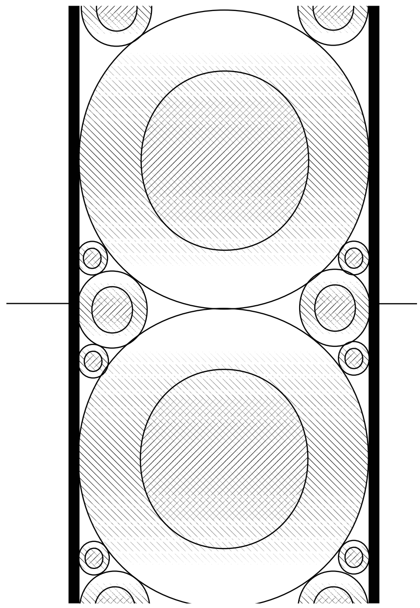

Figure 1: A sketch of a situation which realize the boundary of the conductivity of a mixture of different conductors, Eq.(8). The situation corresponds to dense filling of the whole space with balls with the core made of one of the conductors (the one with larger conductivity for the lower bound, the one with smaller conductivity for the upper one) and with the outer shell made of the other one. Note that the situation does not correspond to what we could call a "disordered" system, but the order (Apollonian packing) is now extremely complex.

A more important thing is the following. Let us consider a composite consisting of insulator and conductor, with $\sigma_1 = 0$ and $\sigma_2 = \sigma$. Rewriting the corresponding expression we get

$$0 \leq \sigma^* \leq \sigma \frac{1-p}{1-p/(d-1)}.$$

Thus, in 1d the conductivity of such a composite has to vanish for any p except for $p = 0$. In $d = 2$ the bounds are still unsatisfactory since it is anyhow clear that $\sigma^* \leq \sigma$ (the weak bound can even be considered as "stupid" since it proposes values of σ^* which might exceed σ). The case $\sigma_1 = 0$ is therefore a very complex one: systems with high contrast show indeed quite peculiar behavior.