

Thermoelectric power in inhomogeneous materials*

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The thermal conductivity and thermoelectric power of an inhomogeneous material subjected simultaneously to gradients of temperature and electric potential are accounted for in terms of an effective-medium theory as well as by numerical simulations in cubic networks with correlated bonds.

I. INTRODUCTION

Transport properties of disordered materials undergoing a metal-nonmetal transition have been of considerable importance in the identification of some of these transitions as occurring via the inhomogeneous transport regime.¹⁻⁷ Within the semi-classical approximation the transport problem becomes equivalent to the calculation of the response functions in a microscopically inhomogeneous medium. Effective-medium theories for the electrical conductivity,⁸⁻¹⁴ the Hall effect,¹⁴ optical properties,^{15,16} and sound velocity^{3(b)} have been invoked for the analysis of experimental data in a variety of microscopically inhomogeneous materials.^{1-7,15,16} It is now well established that the effective-medium theory for the electrical conductivity, the Hall effect and the optical data is adequate for metallic volume fraction C well above the percolation threshold $C^* = 0.145 \pm 0.005$,¹³⁻¹⁸ the effective-medium theory being unreliable in the transition region $C \leq 0.4$ and below.¹³⁻¹⁸ Numerical simulation methods for the conductivity,^{13,17} the magnetoconductivity tensor,¹⁸ and the complex dielectric constant¹⁶ were developed to account for the response functions over the entire C range.

In this paper we continue our program of the study of transport properties of inhomogeneous materials and advance an effective-medium theory together with a generalized numerical-simulation scheme for thermal transport properties, i.e., the thermal conductivity and the thermoelectric power of such disordered materials. An effective-medium theory for the thermal conductivity was provided by Odehlevskii,¹⁰ while Airapetiants¹⁹ attempted an effective-medium theory for the thermoelectric power. The latter treatment does not involve a completely self-consistent configurational averaging. Our effective-medium results, together with numerical simulation data, elucidate the significant features of thermal transport properties in inhomogeneous materials.

II. EFFECTIVE-MEDIUM THEORY FOR THERMAL TRANSPORT

We now present a derivation of a generalized effective-medium theory for a system simultaneously subjected to gradients of temperature and electric potential. We start with the following microscopic equations

$$\vec{j}'_Q = -\kappa' \vec{\nabla} T' + P' T' \vec{\nabla} \varphi', \quad (2.1a)$$

$$\vec{j}' = -\sigma' \vec{\nabla} \varphi' + P' \vec{\nabla} T', \quad (2.1b)$$

which hold locally within the inhomogeneous material. Primed quantities indicate local values. $\vec{j}'_Q$ and $\vec{j}'$ are the heat and electric currents, respectively, and κ' and σ' are the thermal and electrical conductivity. P' is the Peltier coefficient, while φ' and T' are the electrical potential and temperature. The corresponding macroscopic equations are analogous to Eqs. (2.1a) and (2.1b) but with macroscopic, unprimed quantities:

$$\vec{j}_Q = -\kappa \vec{\nabla} T + P T \vec{\nabla} \varphi, \quad (2.2a)$$

$$\vec{j} = -\sigma \vec{\nabla} \varphi + P \vec{\nabla} T. \quad (2.2b)$$

The relation between the macroscopic and microscopic fluxes and forces is

$$\begin{aligned} \vec{j}_Q &= \langle \vec{j}'_Q \rangle, \quad \vec{\nabla} T = \langle \vec{\nabla} T' \rangle, \\ \vec{j} &= \langle \vec{j}' \rangle, \quad \vec{\nabla} \varphi = \langle \vec{\nabla} \varphi' \rangle, \end{aligned} \quad (2.3)$$

where the average can be taken equivalently over all space or over all local configurations at a given point.

From Eqs. (2.2) and (2.3) we get the following equations relating the macroscopic transport coefficients to the microscopic quantities:

$$-\kappa \langle \vec{\nabla} T' \rangle + P \langle T' \vec{\nabla} \varphi' \rangle = -\langle \kappa' \vec{\nabla} T' \rangle + \langle P' T' \vec{\nabla} \varphi' \rangle, \quad (2.4a)$$

$$-\sigma \langle \vec{\nabla} \varphi' \rangle + P \langle \vec{\nabla} T' \rangle = -\langle \sigma' \vec{\nabla} \varphi' \rangle + \langle P' \vec{\nabla} T' \rangle. \quad (2.4b)$$

To carry out an effective-medium theory of the relation between κ , σ , and P and the corresponding

microscopic quantities, we treat the system as though it consisted of a sphere of radius b embedded within a uniform effective-medium characterized by the coefficients κ , σ , and P . The local temperature and potential fields φ' and T' obey the equations

$$\nabla^2 T' = 0, \quad \nabla^2 \varphi' = 0, \quad (2.5)$$

both inside the sphere (region I) and in the effective-medium (region II).

The solutions of Eq. (2.5) for $T'(\mathbf{r})$ and $\varphi'(\mathbf{r})$ are

$$T'(\mathbf{r}) = \begin{cases} T_0 + A'_1 r \cos \theta & \text{(region I),} \\ T_0 + (B_1 r + C'_1 b^3/r^2) \cos \theta & \text{(region II),} \end{cases} \quad (2.6a)$$

$$\varphi'(\mathbf{r}) = \begin{cases} \varphi_0 + A'_2 r \cos \theta & \text{(region I),} \\ \varphi_0 + (B_2 r + C'_2 b^3/r^2) \cos \theta & \text{(region II).} \end{cases} \quad (2.6b)$$

The parameters A'_i , B_i , and C'_i can be determined by the following boundary conditions: (a) the continuity of the potential and temperature at the sphere boundary ϕ

$$T'_I = T'_{II}, \quad \varphi'_I = \varphi'_{II}, \quad r = b; \quad (2.7a)$$

(b) the continuity of the normal components of the electrical and thermal currents at the sphere boundary ϕ

$$(\vec{j}'_Q \cdot \vec{r})_I = (\vec{j}'_Q \cdot \vec{r})_{II}, \quad (\vec{j}' \cdot \vec{r})_I = (\vec{j}' \cdot \vec{r})_{II}. \quad (2.7b)$$

From Eq. (2.7a) we get

$$A'_1 = B_1 + C'_1, \quad A'_2 = B_2 + C'_2. \quad (2.8)$$

According to the effective-medium assumption, in region II $\kappa' = \kappa$, $P' = P$, and $\sigma' = \sigma$. We can therefore recast conditions (2.7b), using Eqs. (2.1) and (2.6) into the following equations:

$$-\kappa' A'_1 + P' T_0 A'_2 = -\kappa (B_1 - 2C'_1) + P T_0 (B_2 - 2C'_2), \quad (2.9a)$$

$$P' A'_1 - \sigma' A'_2 = P (B_1 - 2C'_1 - \sigma (B_2 - 2C'_2)). \quad (2.9b)$$

Equations (2.8) and (2.9) can be solved for A'_i :

$$A'_1 = (1 + M'_{11}) B_1 + M'_{12} B_2, \quad (2.10a)$$

$$A'_2 = M'_{21} B_1 + (1 + M'_{22}) B_2. \quad (2.10b)$$

We now adopt the approximation that κ and σ are zero-order quantities whereas P is a first-order quantity, and obtain

$$M'_{11} = (\kappa - \kappa')/(\kappa' + 2\kappa), \quad (2.10c)$$

$$M'_{22} = (\sigma - \sigma')/(\sigma' + 2\sigma), \quad (2.10d)$$

$$M'_{12} = -\left(\frac{P - P'}{\kappa' + 2\kappa} - \frac{(\sigma - \sigma')(P' + 2P)}{(\kappa' + 2\kappa)(\sigma' + 2\sigma)} \right) T_0, \quad (2.10e)$$

$$M'_{21} = -\left(\frac{P - P'}{\sigma' + 2\sigma} - \frac{(\kappa - \kappa')(P' + 2P)}{(\kappa' + 2\kappa)(\sigma' + 2\sigma)} \right). \quad (2.10f)$$

We now introduce these results into Eq. (2.4b), the consistency conditions for the average electrical current:

$$\begin{aligned} & (-\sigma \langle M'_{21} \rangle + P \langle 1 + M'_{11} \rangle) B_1 + (-\sigma \langle 1 + M'_{22} \rangle + P \langle M'_{12} \rangle) B_2 \\ &= [\langle -\sigma' M'_{21} \rangle + \langle P' (1 + M'_{11}) \rangle] B_1 \\ &+ [-\langle \sigma' (1 + M'_{22}) \rangle + \langle P' M'_{12} \rangle] B_2. \end{aligned} \quad (2.11)$$

The parameters B_1 and B_2 [Eq. (2.6)], are the constant temperature gradient and the constant electric field far away from the sphere. Since the value of P , κ , and σ are independent of the magnitudes of the electric and thermal fields imposed on the sample in any specific experiment, Eq. (2.11) can be split into two separate equations:

$$-\sigma \langle M'_{21} \rangle + P \langle 1 + M'_{11} \rangle = -\langle \sigma' M'_{21} \rangle + \langle P' (1 + M'_{11}) \rangle, \quad (2.12a)$$

$$-\sigma \langle 1 + M'_{22} \rangle + P \langle M'_{12} \rangle = -\langle \sigma' (1 + M'_{22}) \rangle + \langle P' M'_{12} \rangle. \quad (2.12b)$$

Equation (2.12a) can be solved for P in terms of the effective-medium response function σ , κ , and the local quantities κ' , P' , σ' . The final result is

$$\begin{aligned} P &= 3\sigma\kappa \left\langle \frac{P'}{(\kappa' + 2\kappa)(\sigma' + 2\sigma)} \right\rangle \\ &\times \left\langle \left(\frac{\sigma'\kappa + \sigma\kappa' + 2\sigma\kappa - \sigma'\kappa'}{(\kappa' + 2\kappa)(\sigma' + 2\sigma)} \right)^{-1} \right\rangle. \end{aligned} \quad (2.13)$$

The same procedure can be applied to Eq. (2.4a), the consistency condition for the thermal current. An expression for P identical to Eq. (2.13) is obtained. This result is an expression of the Onsager relations between the macroscopic transport coefficients.²⁰ The values of κ and σ in Eq. (2.13) are simply the solutions of the effective-medium-theory (EMT) equations for the thermal conductivity and the electrical conductivity

$$\left\langle \frac{\kappa' - \kappa}{\kappa' + 2\kappa} \right\rangle = 0; \quad \left\langle \frac{\sigma' - \sigma}{\sigma' + 2\sigma} \right\rangle = 0. \quad (2.14)$$

Equations (2.14) result from Eq. (2.12b) within the approximation adopted for the derivation of Eq. (2.10).

The thermoelectric power is derived from P through the relation

$$S = P/\sigma. \quad (2.15)$$

An EMT formula for S in terms of S' , κ' , σ' can be recast as follows:

$$S = 6\kappa\langle S'D' \rangle / (1 - 3\langle \kappa'D' \rangle), \quad (2.16)$$

where

$$D' = \sigma' / (\kappa' + 2\kappa)(\sigma' + 2\sigma) \quad (2.17)$$

and

$$S' = P' / \sigma'. \quad (2.18)$$

Our effective-medium result, Eqs. (2.16)–(2.18), for the thermoelectric power differs from that previously derived by Airapetiants,¹⁹ as the latter treatment did not involve a completely self-consistent averaging procedure.

III. NUMERICAL SIMULATIONS

In the present case we have two local transport equations given by Eqs. (2.1a) and (2.1b). The two relevant continuity equations are

$$\vec{\nabla} \cdot \vec{j}'_Q(\vec{r}) = 0, \quad (3.1)$$

$$\vec{\nabla} \cdot \vec{j}'(\vec{r}) = 0. \quad (3.2)$$

For the numerical simulation of the thermoelectric properties of a binary inhomogeneous system we assign randomly to the bonds of a cubic network

the local values κ_0 , σ_0 , and P_0 with probability C , and the values κ_1 , σ_1 , and P_1 with probability $1 - C$. A schematic description of the cubic network is presented in Fig. 1. The sites $\{r_i\}$ of the network are assigned local temperature and potential values, $\{T_i\}$ and $\{\varphi_i\}$, respectively. The finite difference representation of Eqs. (3.1) and (3.2) is given by the following set of coupled equations for each site r_i of the network:

$$\sum_{\substack{j \\ \text{neighbors of } i}} [-\kappa_{ij}(T_j - T_i) + P_{ij} \frac{1}{2}(T_i + T_j)(\varphi_j - \varphi_i)] = 0, \quad (3.3a)$$

$$\sum_{\substack{j \\ \text{neighbors of } i}} [-\sigma_{ij}(\varphi_j - \varphi_i) + P_{ij}(T_j - T_i)] = 0, \quad (3.3b)$$

where κ_{ij} , P_{ij} , and σ_{ij} are the values of local properties assigned to the bond (r_i, r_j) . The zy faces of the cube represent the electrodes. Each electrode is kept at a constant temperature and a constant potential (see Fig. 1). The initial set of values $\{T_i^{(0)}\}$ are chosen to be linear in the x direction. Equations (3.3a) and (3.3b) are solved by a relaxation procedure as follows:

$$T_i^{(n)} = (1 - \Omega)T_i^{(n-1)} - \Omega \left(\sum_{\substack{j \\ \text{neighbors of } i}} [-\kappa_{ij}T_j^{(m)} + P_{ij} \frac{1}{2}(T_i^{(n-1)} + T_j^{(m)})(\varphi_j^{(m)} - \varphi_i^{(n-1)})] \right) / \sum_j \kappa_{ij}, \quad (3.4a)$$

$$\varphi_i^{(n)} = (1 - \Omega)\varphi_i^{(n-1)} - \Omega \left(\sum_{\substack{j \\ \text{neighbors of } i}} [-\sigma_{ij}\varphi_j^{(m)} + P_{ij}(T_j^{(m)} - T_i^{(n-1)})] \right) / \sum_j \sigma_{ij}. \quad (3.4b)$$

Here n is the order of iteration. The value of m is either n if the site j precedes the site i in the iteration procedure, or $n - 1$ in the reverse case. Ω is an overrelaxation parameter, $1.5 < \Omega < 1.9$. During the iterations all the sites on one electrode keep the constant potential $\varphi = 0$ and temperature $T = T_0$, while on the other electrode $T = T_0 + \Delta T$, $\varphi = \Delta\varphi$ (see Fig. 1). After convergence has been reached, the heat current and electric current densities between the l and $l + 1$ zy planes are given by

$$j_{Ql} = \frac{1}{N_{zy}} \left(\sum [-\kappa_{l+1,l}(T_{l+1} - T_l) + P_{l+1,l} \frac{1}{2}(T_{l+1} + T_l)(\varphi_{l+1} - \varphi_l)] \right), \quad (3.5)$$

$$j_l = \frac{1}{N_{zy}} \left(\sum [-\sigma_{l+1,l}(\varphi_{l+1} - \varphi_l) + P_{l+1,l}(T_{l+1} - T_l)] \right),$$

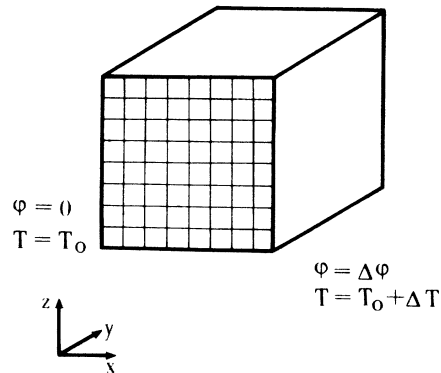


FIG. 1. Schematic description of the cubic network employed for the numerical simulation of the thermoelectric power of inhomogeneous materials. The zy faces of the cube represent the electrodes, while at the other faces cyclic boundary conditions are applied. The average electric and thermal currents flow in the x direction.

where the summation is carried out over all the sites in the l th plane and where N_{xy} is the number of sites in the plane. The convergence can be checked by the continuity conditions

$$\begin{aligned} j_{q_0} &= j_{q_1} = \dots = j_{q_{N-1}} = j_q(\Delta T, \Delta \varphi), \\ j_0 &= j_1 = \dots = j_{N-1} = j(\Delta T, \Delta \varphi). \end{aligned} \quad (3.6)$$

The solution is carried out twice; first for $\Delta T = 0$ and second for a finite value of ΔT . The macroscopic value of P is then given by

$$P = [j(\Delta T, \Delta \varphi) - j(\Delta T = 0, \Delta \varphi)] / \Delta T, \quad (3.7)$$

and the thermoelectric power S is

$$S = P / \sigma, \quad (3.8)$$

while the conductivity is given by

$$\sigma = L j(\Delta T = 0, \Delta \varphi) / \Delta \varphi \quad (3.9)$$

where L is the length of the cubic network. As in the cases of electrical conductivity,¹⁷ dielectric constant,¹⁶ and Hall effect,¹⁸ the numerical simulations were carried out on correlated networks which simulate a continuous inhomogeneous medium.¹⁷ The numerical results for S of a two-component inhomogeneous system with the local values of κ' , P' , and σ' characteristic of Li-NH₃ are presented in Fig. 2, together with the results of the EMT.

These numerical results for the thermoelectric power in this binary system, where the local con-

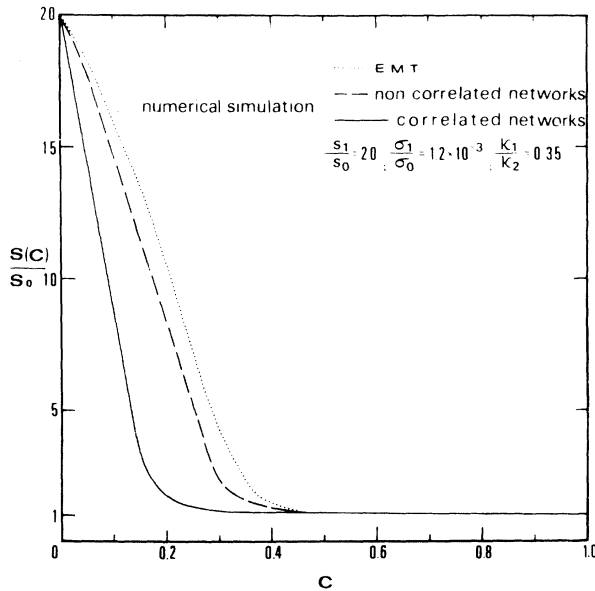


FIG. 2. Thermoelectric power of a binary inhomogeneous material. $S_1/S_0 = 20$, $\sigma_1/\sigma_0 = 1.2 \times 10^{-3}$, $\kappa_1/\kappa_0 = 0.35$.

ductivity is characterized by a large fluctuation, exhibit several interesting features. First, for $C \geq 0.4$ the numerical data for S are in good agreement with the effective-medium theory, as is the case for the electrical conductivity¹⁷ and for the magnetoconductivity tensor.¹⁸ Second, for $C \geq 0.45$, i.e., well above the percolation threshold, $S = S_0$, independent of C . This behavior is characteristic of the bimodal distribution and can be utilized as a diagnostic feature for the identification of such a distribution in microscopically inhomogeneous materials. Thirdly, just above the percolation threshold $C_{\text{EMT}}^* = \frac{1}{3}$ for the effective-medium theory, $C^* = 0.25$ for a noncorrelated network, and¹⁷ $C^* = 0.145 \pm 0.005$ for continuous percolation, S exhibits a pronounced rise with decreasing C .

IV. LIMITING CASES

We now consider the solutions of the EMT and the numerical results for two-component inhomogeneous materials. A particularly simple result can be obtained from the EMT, Eq. (2.16), for the case where

$$\sigma_1 \ll \sigma_0, \quad P_1 \ll P_0. \quad (4.1)$$

For all values of C for which $\sigma_1 \ll \sigma(C)$, i.e., $C \geq 0.5$, we get directly from the EMT result, Eq. (2.16),

$$S(C) = S_0. \quad (4.2)$$

A derivation of Eq. (4.2) from the local continuity equations is given in Appendix A. The conditions $\sigma_1 \ll \sigma_0$, $P_1 \ll P_0$ are obeyed by the values used for calculations and numerical simulations presented in Fig. 2. We note that the result, Eq. (4.2), is reproduced by the numerical simulations over a wider range of metallic volume fraction ($C \geq 0.3$).

In the low metallic concentration range below C^* , a simple result for $P(C)$ and $S(C)$ can be derived from Eq. (2.16) for the case in which

$$\sigma_1 \ll \sigma_0, \quad S_1 \gg S_0, \quad \kappa_1 \sim \kappa_0. \quad (4.3)$$

We get

$$P(C) = P_1 \quad (4.4)$$

or

$$S(C) = \sigma_1 S_1 / \sigma(C) = S_1 (1 - 3C). \quad (4.5)$$

Equation (4.5) has the form

$$S(C) = (S_1 / C_{\text{EMT}}^*) (C_{\text{EMT}}^* - C), \quad (4.6)$$

where $C_{\text{EMT}}^* = \frac{1}{3}$ is the percolation threshold obtained in the EMT. The C dependence of Eq. (4.6) arises entirely from that of the conductivity, which we have shown, is accurately represented by replacing C_{EMT}^* by the true threshold, $C^* = 0.145$, for

continuous percolation, so that

$$S(C) = (S_1/C^*)(C^* - C). \quad (4.7)$$

Condition (4.3) is only roughly obeyed by the values used in Fig. 2. Qualitatively, however, both the EMT and numerical results are characterized by a weak C dependence of P below C^* , while above C^* , $P(C) \sim \sigma(C)$. Equivalently, $S(C)$ is proportional to $\sigma^{-1}(C)$ below C^* and is constant above it. This behavior provides a stringent test of the existence of a binary distribution of values of the local transport coefficients. As the distribution broadens from the sum of two δ functions, the region of curvature in the S -vs- C plot can be expected to spread out.

Cohen and Jortner³ have proposed a model of bimodality of concentration fluctuations in metal-ammonia solutions, particularly in Li-NH₃ solutions and Na-NH₃ solutions, in accounting for the continuous metal-nonmetal transition observed in the range 1–10 mole % metal. In particular, Cohen and Jortner have fitted the EMT for this thermopower described here to the data for Li and Na ammonia solutions. Unfortunately, the experimental data are insufficient for firm conclusions, but there is enough evidence of curvature of S vs C at large C for the Na-NH₃ solutions to infer the existence of some deviation from a strict binary distribution of concentration fluctuations.

APPENDIX A: DERIVATION OF EQ. (4.2)

We shall now derive Eq. (4.2) directly from the local continuity equations without invoking any approximations. The continuity equation for the local electric current, Eq. (3.2), is

$$-\vec{\nabla} \cdot [\sigma(\vec{r}) \vec{\nabla} \varphi(\vec{r})] + \vec{\nabla} \cdot [P(\vec{r}) \vec{\nabla} T(\vec{r})] = 0. \quad (A1)$$

For a binary inhomogeneous medium $\sigma(\vec{r})$ and $P(r)$ both exhibit spatial fluctuations and are characterized by the following bimodal distribution functions for the local values of σ and of P :

$$g(P) = C\delta(P - P_0) + (1 - C)\delta(P - P_1), \quad (A2a)$$

$$g(\sigma) = C\delta(\sigma - \sigma_0) + (1 - C)\delta(\sigma - \sigma_1). \quad (A2b)$$

It is apparent that in the limiting case when $P_1/P_0 = \sigma_1/\sigma_0$

$$P(\vec{r}) = (P_0/\sigma_0)\sigma(\vec{r}). \quad (A3)$$

The local potential field in a sample subjected to both potential and temperature gradient can be considered as a sum of two terms

$$\varphi(\vec{r}) = \varphi^0(\vec{r}) + \delta\varphi(\vec{r}), \quad (A4)$$

where $\varphi^0(r)$ is a solution of the local continuity equation in the case where the average temperature gradient vanishes

$$\vec{\nabla}[\sigma(\vec{r}) \vec{\nabla} \varphi^0(\vec{r})] = 0. \quad (A5)$$

We now have from Eqs. (A1), (A4), and (A5)

$$-\vec{\nabla}[\sigma(\vec{r}) \vec{\nabla} \delta\varphi(\vec{r})] + \vec{\nabla}[P \cdot \vec{\nabla} T(\vec{r})] = 0. \quad (A6)$$

For values of C for which $\sigma(C) \gg \sigma_1$, $\sigma(C)$ does not depend on the value of σ_1 as long as $\sigma_1 \ll \sigma_0$. Similar behavior can be expected for $P(C)$. Under the conditions expressed by Eq. (2.1), the results in the region $C \gtrsim C^* + 0.1$ will therefore not be affected if we assume that $\sigma_1/\sigma_0 = P_1/P_0$. Under this assumption, Eq. (A4) holds and Eq. (A6) can be recast in terms of a new potential field, $\Phi(r)$

$$\vec{\nabla}[\sigma(\vec{r}) \vec{\nabla} \Phi(\vec{r})] = 0, \quad (A7a)$$

where

$$\Phi(\vec{r}) = -\delta\varphi(\vec{r}) + (P_0/\sigma_0)T(\vec{r}). \quad (A7b)$$

Since Eq. (A7a) is analogous to Eq. (A5) we may conclude that

$$\Phi(\vec{r}) \propto \varphi^0(\vec{r}). \quad (A8)$$

Now, utilizing the relation

$$\sigma \langle \vec{\nabla} \varphi \rangle = \langle \sigma(\vec{r}) \vec{\nabla} \varphi^0(\vec{r}) \rangle, \quad (A9)$$

where σ is the macroscopic conductivity and $\langle \vec{\nabla} \varphi \rangle$ the macroscopic potential gradient, together with Eq. (2.4b) one gets the following relation for $S(C)$:

$$S(C) = \frac{P(C)}{\sigma(C)} = \frac{\langle \sigma(\vec{r}) \vec{\nabla} \Phi(\vec{r}) \rangle}{\langle \sigma(\vec{r}) \vec{\nabla} \varphi^0(\vec{r}) \rangle}. \quad (A10)$$

From Eq. (A8) it is apparent that $\langle \sigma(r) \vec{\nabla} \Phi(r) \rangle$ and $\langle \sigma(r) \vec{\nabla} \varphi^0(r) \rangle$ exhibit the same C dependence, whereupon $S(C)$ is independent of C , i.e., $S(C) = S_0$ for $C > C^* + 0.1$, or so.

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