

Understanding the doping dependence of the conductivity of conjugated polymers: Dominant role of the increasing density of states and growing delocalization

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In variable-range-hopping theories for the dc conductivity, the extension of sites where the charges are located and the energy dependence of the density of states (DOS) are usually neglected. We show that these dependences are the dominant factors for understanding the strong doping dependence, and present an analytical theory for arbitrary DOS. We verify the theory with systematic data over a broad range of temperature and doping for FeCl₃-doped poly(*p*-phenylene vinylene). By combining theory and data, we reconstruct the energy-dependent DOS and the extension of sites.

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The strong increase in conductivity with doping of conjugated polymers was the first essential breakthrough that made the field of polymer electronics the revolutionary field that it is today. Although the fact has been demonstrated and discussed many times since,¹ the steeply nonlinear functional relation between dopant concentration and conductivity in the insulating state has not been consistently explained.²⁻⁵ For the more frequently studied and equally steep temperature dependence of the conductivity,⁵⁻⁸ various approaches exist, which have in common that some kind of phonon-assisted hopping between localized states allows the dc transport. In these models disorder, correlations and (bi)polaron formation can play a role as well and often simplifying assumptions have been made about the shape of the density of states (DOS).^{1,5,9-13} Because of these differences, it will be helpful to follow a more general approach, the results of which might also guide more detailed microscopic descriptions. Here we start from Mott's three-dimensional (3D) variable range hopping (VRH) and allow for a spatial extension of the localized states that were originally approximated as dimensionless points. It appears that without specifying the exact nature of the charge carriers involved in the conductivity, we can clarify the relation between conductivity and doping level in the nonmetallic state for the common case, where 3D charge transport prevails already at the lowest doping levels.¹⁴ The major outcomes are as follows.

(1) A fully general analytical result [see Eq. (4)], identifying how the strong dopant dependence relates to two dominant effects: the increasing DOS at higher concentrations, and the growth of the delocalized regions. This result not only gives mechanistic insight that was so far absent, but is mathematically applicable to any shape of the DOS.

(2) An extension [see Eq. (5)], accounting for the dopant/delocalization dependence, of the classical result of Mott, which has so far been the reference for modeling the *T*-dependent variable-range-hopping conductivity in doped polymers.

(3) Successful verification of the theory with very precise and systematic data over a broad range of concentration and temperature, using FeCl₃-doped poly(*p*-phenylene vinylene) (PPV) as paradigm.

(4) Actual reconstruction, from the combined theory and data, of the energy-dependent DOS of the doped polymer. Although these results are derived for the insulating state, we expect them to be relevant for our understanding of the metal-insulator transition and the metallic phase of these conjugated polymers as well.

OC₁C₁₀-PPV was doped in solution with iron(III)chloride, FeCl₃. Ideally, the following redox reaction should take place: PPV + 2FeCl₃ → PPV⁺ + FeCl₂ + FeCl₄⁻. The doping level *c* is defined as the number of carriers per monomer.¹⁵ We refer for more details to Ref. 14. Under ambient conditions, the conductive properties of the films are stable over several weeks.

The *T* dependence of σ is presented in Fig. 1, where σ is plotted versus $T^{-1/4}$ on a log-linear scale. At sufficiently low *T*, Mott's law $\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/4}]$ for three-dimensional VRH holds.¹⁶ Such a *T* dependence of σ has been frequently reported in doped conjugated polymers,⁵⁻⁸ and is suggestive of thermally activated tunneling of carriers between localized states in a constant density of states. As in other conjugated polymers,²⁻⁵ σ increases steeply with doping level: by increasing *c* from 0.005 to 0.2, σ increases by

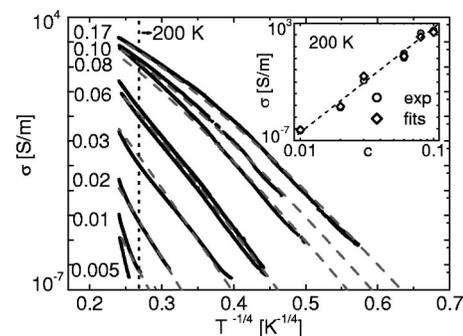


FIG. 1. (a) σ vs $T^{-1/4}$ for $0.005 < c < 0.17$ (two samples have *c* close to 0.06). Doping levels are expressed per monomer. At low *T*, Mott's law $\sigma(T) = \sigma_0 \exp[-(T_0/T)^{1/4}]$ for three-dimensional VRH holds. Dashed lines are fits discussed in the text. Inset shows the powerlike dependence of σ for $0.01 \leq c \leq 0.1$ at 200 K: $\sigma \propto c^8$ (dashed).

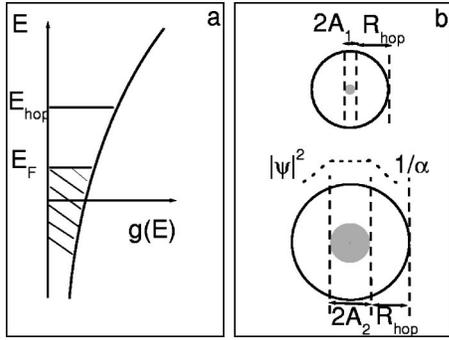


FIG. 2. (a) E vs $g(E)$. States within E_{hop} and $E_F(c)$ are available for hopping (b) $A(c)$. With increasing extent A of the localized states the number of available states, within a given R_{hop} increases. The typical decay length of the electron density ψ^2 is $1/\alpha$.

seven orders of magnitude. At high T , deviations from Mott's law occur: the low- c samples reveal a stronger, and the high- c samples a weaker T dependence of σ , see Fig. 1.

Qualitatively, the strong c dependence of σ can be understood as follows. Due to disorder and self-trapping (polarons), the electronic states are spatially localized and distributed in energy (E). Charge transport occurs by means of VRH. Two contributions to $\sigma(c)$ can be considered. First, in conjugated polymers the density of (localized) states $g(E)$ is energy dependent as schematically indicated in Fig. 2(a).^{9,12,17} When filling such a DOS, more states within a given hopping energy $\epsilon = E_{\text{hop}} - E_F(c)$ become available and this enhances σ exponentially. Also doping-induced states near E_F result in a similar increase of σ . Second, the size of the localized regions (at least a monomer) may grow with increasing c (and thus E_F) as well. The rationale behind this is that states at high E are less strongly bound by the random potential, i.e., are spatially more extended.¹⁸ As the number of states within a given hopping distance R from these finite-size localized sites increases with the localization volume, see Fig. 2(b), σ increases strongly as well. Note that σ of the high- c samples is only an order of magnitude below Mott's minimum metallic conductivity at high T , i.e., a point model of the localized states cannot be expected to hold.

For the peculiar T dependence of σ , we have to keep in mind that at low c the hopping energy is relatively large since $g(E_F)$ is low. If $g(E_{\text{hop}}) > g(E_F)$, more states are available for the hopping process than expected for constant g and also nearest-neighbor hops become more important: σ will be activated (e.g., for $c=0.01$ the activation energy is around 0.5 eV). At high c , $g(E_F)$ is larger resulting in smaller hopping distances, and thus the nonzero extent of the localized states comes into play: within a given hopping distance more states are available and the hop activation energy will decrease. This explains the weaker T dependence of σ observed at high T and high c .

We now derive a VRH expression for $\sigma(c)$ in a system with an arbitrary shape of $g(E)$ and volume V_0 of the localized region. We consider a carrier located at the Fermi level. The squared wave function decays within a length $1/\alpha$ (in point-site models $1/\alpha \gg A$, and $L=1/\alpha$ is referred to as the localization length). The hopping probability depends expo-

nentially both on the hopping distance R between the localized regions and the activation energy $(E - E_F)$.¹⁹ The density of final sites \mathcal{N} that can be reached with activation energy less than $E - E_F$ is given by $\mathcal{N}(E, E_F) = \int_{E_F}^E g(E') dE'$. Mott's criterion states that σ is governed by those hops for which E and R are such that about one state lies within a volume V , defined by: $V\mathcal{N} \approx 1$ [hence $V = V(E, E_F)$].¹⁶ For the moment, R is a unique function, to be specified later, of V and of some length A : $R(V, A) = R(E, E_F, A)$. The conductivity can then be written as^{16,20}

$$\sigma = \sigma_0 \exp[-\alpha \tilde{R} - \beta(\tilde{E} - E_F)] \quad (1)$$

with $\beta = 1/(k_B T)$, and σ_0 a prefactor. The optimal hop energy \tilde{E} and associated hop distance \tilde{R} is obtained if $\alpha R + \beta(E - E_F)$ is minimal or $\alpha(\partial R / \partial E)_{E_F, A} + \beta = 0$ for $E = \tilde{E}$. Differentiation of $V\mathcal{N} \approx 1$ to E gives $(\partial / \partial E)_{E_F, A} V\mathcal{N} = 0$. The condition for \tilde{E} then becomes

$$\frac{1}{V^2} (\partial V / \partial R)_A = \frac{\alpha}{\beta} g(E) \quad (2)$$

for $E = \tilde{E}$. These equations establish the optimal hopping energy $\tilde{E} = E(\beta, E_F, A)$ and hopping distance $\tilde{R} = R[\tilde{E}(\beta, E_F, A), E_F, A]$, which yield the system's conductivity according to Eq. (1). The conductivity depends on c via E_F , A , and σ_0 .

To get more insight into these relations, let us study the dependence on c via E_F and A explicitly.

$$\left(\frac{\partial \ln(\sigma / \sigma_0)}{\partial c} \right)_\beta = \left(\frac{\partial \ln(\sigma / \sigma_0)}{\partial E_F} \right)_{\beta, A} \frac{dE_F}{dc} + \left(\frac{\partial \ln(\sigma / \sigma_0)}{\partial A} \right)_{\beta, E_F} \frac{dA}{dc}. \quad (3)$$

Using Eq. (1), at optimum the first term on the right can be rewritten as $-\alpha(\partial \tilde{R} / \partial E_F)_{\beta, A} - \beta(\partial \tilde{E} / \partial E_F)_{\beta, A} + \beta = -\alpha(\partial \tilde{R} / \partial E_F)_{\tilde{E}, A} - \alpha(\partial \tilde{R} / \partial \tilde{E})_{E_F, A}(\partial \tilde{E} / \partial E_F)_{\beta, A} - \beta(\partial \tilde{E} / \partial E_F)_{\beta, A} + \beta = -\alpha(\partial \tilde{R} / \partial E_F)_{\tilde{E}, A} + \beta = \beta[1 - g(E_F)/g(\tilde{E})]$.²¹ In the last step we used the explicit dependence of \tilde{R} on E_F via $\tilde{V}(\tilde{E}, E_F)$, which leads to $(\partial \tilde{R} / \partial E_F)_{\tilde{E}, A} = \tilde{V}^2 g(E_F)(\partial \tilde{R} / \partial V)_A = (\beta/\alpha)g(E_F)/g(E)$. Following similar arguments, we rewrite the second term as $-\alpha(\partial \tilde{R} / \partial A)_{\beta, E_F} - \beta(\partial \tilde{E} / \partial A)_{\beta, E_F} = -\alpha(\partial \tilde{R} / \partial A)_{\tilde{E}, E_F} - \alpha(\partial \tilde{R} / \partial \tilde{E})_{A, E_F}(\partial \tilde{E} / \partial A)_{\beta, E_F} - \beta(\partial \tilde{E} / \partial A)_{\beta, E_F} = -\alpha(\partial \tilde{R} / \partial A)_{\tilde{E}, E_F} = \alpha[1 - V'_0(A)/V'_0(A + \tilde{R})]$. For the last, line we have to realize that \tilde{R} is a function of $\tilde{V}(\tilde{E}, E_F)$ and A only, and hence $(\partial R / \partial A)_V(\partial A / \partial V)_R(\partial V / \partial R)_A = -1$. We also made a more specific assumption $V = V_0(A + R) - V_0(A)$, still with arbitrary V_0 , see above. The final expression for the dependence of σ/σ_0 on c then becomes

$$\left(\frac{\partial \ln(\sigma/\sigma_0)}{\partial c}\right)_\beta = \beta \left[\frac{1}{g(E_F)} - \frac{1}{g(\bar{E})} \right] + \alpha \left[\frac{1}{V_0'(A)} - \frac{1}{V_0'(A+\bar{R})} \right] \frac{dA}{dc}, \quad (4)$$

where we replaced dE_F/dc in Eq. (3) by $1/g(E_F)$. This expression is particularly suited to illustrate the c dependence of σ . In the limit of low doping [$A \ll R$, hence $V_0'(A+\bar{R}) \gg V_0'(A)$], the last term reduces to $\alpha(dA/dc)$ or $\sigma \propto \exp[\alpha A(c)]$. At sufficiently low temperature, we can replace the difference $g(E_F) - g(\bar{E})$ by $(\bar{E} - E_F)g'(E_F)$ which can be neglected. It means that Mott's formula is recovered:

$$\sigma = \sigma_0(c) e^{\alpha A(c)} e^{-[T_0(c)/T]^{1/4}} \quad (5)$$

with the important addition of the factor $e^{\alpha A(c)}$: At a given temperature, the growth of the localized regime determines for an appreciable part the increase in conductivity. (In the limit that $V_0(A)$ can be neglected compared to $V_0(A+R)$, the exponential prefactor of Eq. (5) also directly follows from the usual Mott argument, if we replace the hopping variable R by $A+R$. Outside the localized region the wave function ψ [see Fig. 2(b)] decays similarly, but inside it grows with the same exponential factor as added in Eq. (5). A power-law dependence of σ on c , as is often suggested (and also found in our data, where around 200 K $\sigma \propto c^p$ with p around 8, see Fig. 1), then implies a logarithmic dependence of A on c . If the first term in Eq. (4) dominates, expected for $g(E_F) \ll g(\bar{E})$ relevant for a Gaussian or exponentially growing density of states,^{9,12} $\partial c/\partial \ln(\sigma/\sigma_0)$ is a direct measure of $g(E_F)$.

We now apply this model to reconstruct the c dependence of A and the density of states as function E_F for the FeCl_3 -doped PPV. To obtain an analytic solution, we assume a (nearly) constant density of states $\mathcal{N}(E, E_F) \approx (E - E_F)g$ and spherically symmetric volumes $V = V_0(A+R) - V_0(A)$ with $V_0(A) = (4\pi/3)A^3$. Under these conditions, $V\mathcal{N} \approx 1$ gives $(E - E_F) = (A + \bar{R})(\alpha/4\pi g\beta)^{0.5}$, while Mott's criterion leads to $(\bar{E} - E_F) = 3/[4\pi g(\bar{R}^3 + A^3 + 3A^2\bar{R} + 3A\bar{R}^2)]$. Subtracting these two equations gives \bar{R} and by substitution of \bar{R} in $\bar{E} - E_F$ we obtain σ from Eq. (1).²² The fits shown in Fig. 1 are based on this solution, which for an appreciable range in c (the lower values) and T (lower temperatures) has to coincide with the predictions of Eq. (5).

Figure 3(a) shows $g(E_F)$ as function of c according to Eq. (5) with $k_B T_0 \propto \alpha^3/g$.²³ The T_0 's are obtained from the low-temperature tails in Fig. 1. The values for $c = 0.01, 0.02, 0.03, 0.06, 0.08, 0.10$, and 0.17 are, respectively, 1.8×10^8 K, 1.2×10^8 K, 7.5×10^7 K, 5.4×10^7 K, 3.3×10^7 K, 3×10^7 K, and 2.4×10^7 K, while a rough estimate at $c = 0.005$ gives a value of the order of 2.5×10^8 . Absolute values of $g(E)$ require an estimate of α^{-1} , which is taken as 0.2 nm,²⁴ the volume of a monomer (1 nm³) and the proportionality constant (here we take 12 as will be justified later). With these values, T_0 of 10^8 K corresponds to $g \approx 1 \times 10^{44}$ states/m³ J. This converts to $g \approx 2 \times 10^{-2}$ states/

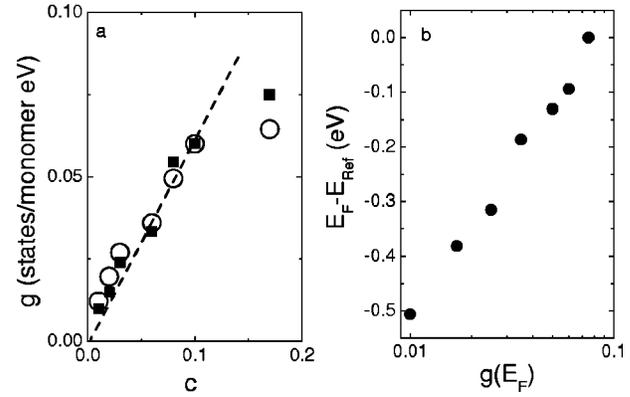


FIG. 3. (a) $g(E_F)$ as a function of doping level. $g(E_F)$ is calculated from Eq. (5) (open circles) and from the model discussed in the text (closed squares). (b) $(E_F - E_{\text{Ref}})$ vs $g(E_F)$. Data are scaled to reproduce the activation energy of 0.5 eV deduced from the high- T data for $c = 0.01$, see Fig. 1.

eV monomer. $g(E_F)$ values from T_0 (squares) and the fits to the full expression given above (circles) agree when we adjust the proportionality constant to 12, which compares well with theoretical estimates.²³ The found dependence of $g(E_F)$ on c is almost linear; the drawn line in Fig. 3(a) corresponds to $g(E_F, c) = 0.6c$. The energy density of states per monomer g_m as function of E_F [see Fig. 3(b)] can be calculated using $E_{\text{Ref}} - E_F = -\int_{c_{\text{Ref}}}^c [1/g_m(c)] dc$, which follows from $dE_F/dc = 1/g_m(E_F)$. The values found are too high to be realistic (order of eV), which is not surprising in view of the crude assumptions made (especially the value of α enters strongly). We scaled the energy scale [vertical axis in Fig. 3(b)] to reproduce the activation energy of 0.5 eV found from the high- T data of $c = 0.01$, see Fig. 1. Note that an increase of g with c might also result if dopants introduce additional sites or energy states to which hopping can occur. If so, the reconstructed dependence of $g(E)$ on c , shown in Fig. 3(a), remains valid, but the plot of E versus $g(E_F)$ loses its validity as it requires $g(E)$ to be c independent.

Although the almost linear increase of $g(E_F)$ with c explains the T dependence at low temperature, it cannot explain the strong c dependence of the data or the deviations at higher temperature. For that purpose, not only the increasing values of $g(E)$ but also of A with c have to be taken into account. Also σ_0 is expected to depend slightly on c , e.g. for a flat density of states $\sigma_0 \propto g(E, E_F)^{1/2}$.²³ Here we took its value constant ($\sigma_0 = 2 \times 10^5$ S/m). The A values, see Fig. 4(a), range between 1 and 5 nm and follow the logarithmic dependence expected from the power-law behavior seen in the inset of Fig. 1. Using voltage modulated millimeter-wave spectroscopy on light emitting diodes of chemically undoped PPV, a similar localization volume was found.²⁵ Within the model, a saturation of A at high doping levels is not surprising as the localized regions start to consume the total available volume of the polymer. At low doping levels, the saturation length is set by the conjugation length of at least a few monomers along the chain and a monomer in the perpendicular direction; because anisotropy is not included in this simple model, the effective size has to exceed that of a

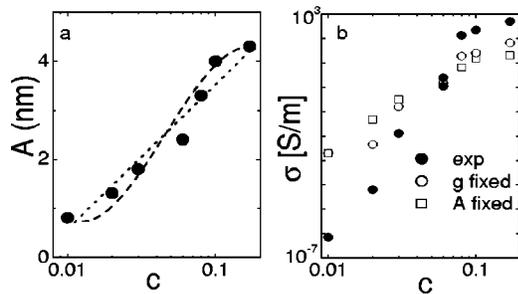


FIG. 4. (a) $A(c)$ from the fits in Fig. 1 with $\sigma_0 = 2 \times 10^5$ S/m [for $g(c)$, see Fig. 3]. The dashed line accounts for the saturation at low- and high- c values; the dotted line is the logarithmic dependence, expected from the power-law behavior in the inset of Fig. 1. (b) The contributions to $\sigma(c)$ from the c dependence of A with fixed g and g with fixed A at 200 K.

monomer. In Fig. 4(b), we compare the contributions of $g(c)$ and $A(c)$ to $\sigma(c)$ for $T = 200$ K, where we kept the values at $c = 0.06$ as turning point: the $\sigma(c)$ values were calculated using the calculated values of $g(A)$ with $A(g)$ fixed to 3.5 nm ($g = 2.4 \cdot 10^{44} / \text{m}^3 \text{ J}$). Both contributions appear to have a similar effect.

In short, we have shown that for an explanation of the c

and T dependence of σ in conjugated polymers such as PPV, it is essential to take the c dependence of both $g(E)$ and A into account. The derived equations are valid for an arbitrary DOS. For a quantitative description of the data set, which covers a wide range in c and T , Eq. (5) is a good starting point. The growing values of A and g contribute equally to the increase by about eight orders of magnitude in σ if c changes from 0.01 to 0.1. These results are not only important from a fundamental point of view, but for applications dealing with highly conducting polymers as well. It still remains a challenge to relate the extracted parameters to a specific microscopic model for the conduction in these systems (e.g., metallic islands, extended (bi)polaronic states, etc.). The present study provides additional boundary conditions on such refined models, although complete testing would require input from other experiments, such as optical spectroscopy, which probe the charge transport on shorter length and time scales.

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- ¹A.J. Heeger, S. Kivelson, J.R. Schrieffer, and W-P. Su, *Rev. Mod. Phys.* **60**, 781 (1988).
- ²C.K. Chiang, C.R. Fincher, Jr., Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, and A.G. MacDiarmid, *Phys. Rev. Lett.* **39**, 1098 (1977).
- ³Y. Cao, P. Wang, and R. Qian, *Macromol. Chem. Phys.* **186**, 1093 (1985).
- ⁴D.M. de Leeuw, *Synth. Met.* **55-57**, 3597 (1993).
- ⁵R. Menon, C.O. Yoon, D. Moses, and A.J. Heeger, in *Handbook of Conducting Polymers*, 2nd ed., (Dekker, New York, 1998).
- ⁶F. Zuo, M. Angelopoulos, A.G. MacDiarmid, and A.J. Epstein, *Phys. Rev. B* **39**, 3570 (1989).
- ⁷J. Joo, Y.C. Chung, J.-K. Lee, J.K. Hong, W.P. Lee, S.M. Long, A.J. Epstein, H.S. Woo, K.S. Lang, and E.J. Oh, *Synth. Met.* **84**, 831 (1997).
- ⁸B. Sanjai, A. Raghunathan, T.S. Natarajan, G. Rangarajan, S. Thomas, P.V. Prabhakaran, and S. Venkatachalam, *Phys. Rev. B* **55**, 10 734 (1997).
- ⁹H. Bässler, *Phys. Status Solidi B* **175**, 15 (1993).
- ¹⁰L. Zuppiroli, M.N. Bussac, S. Paschen, O. Chauvet, and L. Furro, *Phys. Rev. B* **50**, 5196 (1994).
- ¹¹S.V. Novikov, D.H. Dunlap, V.M. Kenkre, P.E. Parris, and A.V. Vannikov, *Phys. Rev. Lett.* **81**, 4472 (1998).
- ¹²S.D. Baranovskii, H. Cordes, F. Hensel, and G. Leising, *Phys.*

- Rev. B* **62**, 7934 (2000).
- ¹³A.B. Kaiser, *Rep. Prog. Phys.* **64**, 1 (2001).
- ¹⁴We investigated the transition from 1D to 3D in J.A. Reedijk *et al.*, *Phys. Rev. Lett.* **83**, 3904 (1999).
- ¹⁵Mössbauer experiments indicate that this holds for FeCl₃-doped poly(dialkoxy thiophene), see Ref. 15.
- ¹⁶N.F. Mott, *Philos. Mag.* **19**, 835 (1969).
- ¹⁷M.C.J.M. Vissenberg and M. Matters, *Phys. Rev. B* **57**, 12 964 (1998).
- ¹⁸The exponential decay of $|\psi^2|$ outside the delocalized area $1/\alpha$ is assumed to be c independent.
- ¹⁹A. Miller and E. Abrahams, *Phys. Rev.* **120**, 745 (1960).
- ²⁰V. Ambegaokar, B.I. Halperin, and J.S. Langer, *Phys. Rev. B* **4**, 2612 (1971).
- ²¹See, e.g., L. E. Reichl, *A Modern Course in Statistical Physics* (Edward Arnold, London, 1997), p. 13.
- ²²The analytic solutions obtained by, e.g., Maple or Mathematica, are straightforward, but too long for showing.
- ²³H. Böttger and V. V. Bryksin, *Hopping Conduction in Solids* (Akademie Verlag, Berlin, 1985).
- ²⁴H.C.F. Martens, P.W.M. Blom, and H.F.M. Schoo, *Phys. Rev. B* **61**, 7489 (2000).
- ²⁵H.C.F. Martens, O. Hilt, H.B. Brom, P.W.M. Blom, J.N. Huiberts, and H.F.M. Schoo, *Phys. Rev. Lett.* **87**, 086601 (2001).