

LETTER TO THE EDITOR

Macroscopic disorder and the metal–insulator transition in conducting polymers

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Abstract. We describe a simple model for treating the frequency-dependent conductivity $\sigma_e(\omega)$ and dielectric function $\text{Re } \epsilon_e(\omega)$ of a quasi-one-dimensional conducting polymer. The polymer is modelled as a composite medium consisting of spherical regions of ordered polymer, randomly distributed in a much more disordered polymer host. Within each spherical region, the polymer chains are highly oriented, but the axis of orientation varies randomly from sphere to sphere. The disordered host is assumed to be isotropic, but with a conductivity which depends on the connectivity of the polymer chains in the host. $\sigma_e(\omega)$ and $\text{Re } \epsilon(\omega)$, as calculated from this model using a suitable effective medium approximation, reproduce all the main experimental features associated with the metal–insulator transition in these polymers.

Highly conducting polymers have been the subject of intense recent interest [1–6]. Detailed investigation of the temperature and frequency dependence of the dielectric response in these systems has led to the discovery of metallic behaviour and a related insulator–metal transition in doped polypyrrole and polyaniline [5, 6]. This transition is expressed by a dramatic change in the qualitative behaviour of the dielectric coefficient ϵ , depending on the static electrical conductivity σ . In one type of sample, σ decreases sharply at low frequencies, and has a very low static value. At higher frequencies in these samples, there is a peak in the conductivity which moves towards lower frequencies as the d.c. conductivity increases. The dielectric response $\epsilon_1(\omega) \equiv \text{Re } \epsilon(\omega)$ of these samples is typical of ordinary dielectric materials, namely, it is positive at all frequencies. Furthermore, the dielectric coefficient increases with decreasing frequency, and this increase is sharper in samples with higher conductivities. The second type of sample is characterized by larger conductivities which do not fall towards zero at low frequencies. Instead, they either stay roughly constant or even increase at very low frequencies. These samples also exhibit a peak in the a.c. conductivity that continues to move towards lower frequencies as the d.c. conductivity increases. The dielectric response of these samples exhibits three zero crossings, leading to two frequency bands of negative dielectric coefficient. One band appears at very low frequencies, where $\epsilon_1(\omega)$ attains large negative values. A smaller and shallower band appears at higher frequencies. Both bands are wider and deeper in high-conductivity samples. Between these two bands of negative ϵ lies an intermediate frequency range of positive dielectric coefficient. The value of $\epsilon_1(\omega)$ in this regime increases with increasing conductivity.

In recent experimental studies, this conductivity-dependent transition, from a dielectric to metallic behaviour, is attributed to percolation in the presence of inhomogeneous

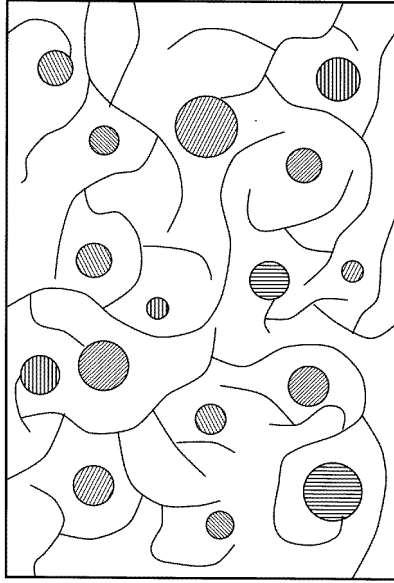


Figure 1. Schematic representation of a random suspension of uniaxial inclusions in an isotropic host. In samples of conducting polymers both the inclusions and the host are made from chains of the same polymer. Inside the inclusions, these chains are aligned in parallel. Their distribution of orientations in the amorphous host is highly disordered and is represented here by the wispy lines around the ordered inclusions.

disorder [6]. Specifically, it is conjectured that the observed behaviour may be explained by the existence of three-dimensional metallic regions embedded in disordered quasi-one-dimensional regions with strong localization effects. Both regions are made up of the same polymer chains and are distinguished only by having different degrees of three-dimensional ordering. In this letter we propose a simple model of macroscopic disorder which incorporates these two basic elements as different components of a composite material. Similar microgeometric models [7] have been used previously to investigate the mechanism for transport in conducting polymers. We use the model to calculate the macroscopic dielectric response of such systems, and to investigate the percolation induced insulator–metal transition. The model leads to a dielectric behaviour that reproduces all the important features of the experimental results.

Our model for the microstructure of conducting polymers includes two basic components (see figure 1). The first component is a collection of randomly distributed spheres. Inside each sphere, the polymer chains are assumed to be ordered parallel to each other. Macroscopically, these spheres are viewed as highly anisotropic particles with dielectric axes defined by the direction of the polymer chains. They have a high conductivity in the direction of the principal dielectric axis and low conductivities in the two perpendicular directions. The dielectric tensor $\tilde{\epsilon}_s$ of these spherical inclusions is assumed to be given by $\tilde{\epsilon}_s = R_{\theta\phi} \tilde{\epsilon} R_{\theta\phi}^T$, where

$$\tilde{\epsilon} = \begin{pmatrix} \epsilon_{\perp} & 0 & 0 \\ 0 & \epsilon_{\perp} & 0 \\ 0 & 0 & \epsilon_{\parallel} \end{pmatrix} \quad (1)$$

is a uniaxial tensor and $R_{\theta\phi}$ is a rotation matrix which specifies the orientation of the

inclusion and varies from inclusion to inclusion. The second component of the model is the host within which the inclusions are embedded. The host is made up of a disordered collection of polymer chains. The orientation of each chain is assumed to vary independently of its neighbours, on length scales that are smaller than the dimensions of the spherical inclusions. Macroscopically, this collection of randomly oriented polymers is homogeneous and isotropic. Its properties may therefore be described by an effective scalar dielectric coefficient ϵ_h .

The macroscopic properties of this composite system can be calculated using the Maxwell–Garnett (MG) approximation [8] (also known as the Clausius–Mosotti approximation). This is one of the most widely used methods for calculating the bulk dielectric properties of inhomogeneous materials [9, 10]. It is most appropriate when one of the components can be considered as a host in which inclusions of the other component are embedded. In this approximation, the field induced in the uniform host by a single spherical or ellipsoidal inclusion is treated exactly, while the distortion of that field by the electrostatic interaction between the different inclusions is approximated. This distortion is caused by the charge dipoles and higher multipoles induced by one inclusion in the other inclusions. Of these multipoles, the induced dipole moments cause the longest-range distortions. The MG approximation therefore includes their average effect, resulting in a uniform field inside all the inclusions. The MG approach has been extensively used for studying the properties of two-component mixtures of isotropic materials with scalar dielectric coefficients. In this letter we use a variant of this approach that is applicable to mixtures of anisotropic inclusions [11].

To describe this approach, we will consider a parallel plate condenser whose plates are large enough that edge effects can be neglected. The condenser is filled by a homogeneous medium with a scalar dielectric constant ϵ_h in which non-overlapping spheres with a tensor dielectric coefficient $\tilde{\epsilon}_s$ are randomly distributed. A voltage is applied between the condenser plates in such a way that the volume averaged field in the system is E_0 . The average field acting on each inclusion is not the applied field E_0 , but the well known Lorentz local field E_l [9]. The difference between E_l and E_0 is due to the correlations between the positions of different spheres arising from the fact that they are prohibited from overlapping. Using this correction, the dipolar interaction between the inclusions is taken into account in an averaged way. A simple method of calculating E_l , usually referred to as the excluded-volume approach, was proposed by Bragg and Pippard [12]. This approach starts from the fact that E_0 is the space-averaged field over the entire system, including both the inside and the outside of the inclusions. This condition leads to a simple relation between the average fields in the host E_l and the inclusions E_s , namely

$$f \langle E_s \rangle + (1 - f)E_l = E_0 \quad (2)$$

where f is the volume fraction of inclusions, and the angular brackets denote an average over the volume of the inclusions. Solving the electrostatic problem for a single sphere immersed in a uniform field E_l , we find that the field inside the inclusion satisfies the relation

$$D_s + 2\epsilon_h E_s = 3\epsilon_h E_l \quad (3)$$

where $D_s = \tilde{\epsilon}_s E_s$ is the uniform displacement field inside the inclusion. Solving equations (2) and (3), we find for the volume-averaged polarization

$$\langle P \rangle = \frac{f}{4\pi} \left\langle \frac{\tilde{\epsilon}_s - \epsilon_h I}{\tilde{\epsilon}_s + 2\epsilon_h I} \right\rangle_{\theta\phi} \frac{3\epsilon_h E_0}{(1 - f) + 3f\epsilon_h \left\langle (\tilde{\epsilon}_s + 2\epsilon_h I)^{-1} \right\rangle_{\theta\phi}} \quad (4)$$

and the volume-averaged displacement field $D_0 = \epsilon_h E_0 + 4\pi \langle P \rangle$. Here, the angular brackets $\langle \rangle_{\theta\phi}$ denote an average over the dielectric tensor orientation inside the inclusions. The bulk effective dielectric tensor, defined as the ratio of D_0 to E_0 , is therefore

$$\tilde{\epsilon}_e = \epsilon_h I + 3f\epsilon_h \left\langle \frac{\tilde{\epsilon}_s - \epsilon_h I}{\tilde{\epsilon}_s + 2\epsilon_h I} \right\rangle_{\theta\phi} \frac{1}{(1-f) + 3f\epsilon_h \left\langle (\tilde{\epsilon}_s + 2\epsilon_h I)^{-1} \right\rangle_{\theta\phi}}. \quad (5)$$

This is the Maxwell–Garnett result for a composite of anisotropic inclusions embedded in an isotropic host. It depends on the type of anisotropy of the tensor $\tilde{\epsilon}$ and on the orientation distribution function for the rotation matrices $R_{\theta\phi}$. In a mixture of randomly oriented uniaxial inclusions, this distribution is uniform over solid angles. In this case the composite as a whole should be isotropic, with a scalar dielectric coefficient. Carrying out the averaging in equation (5) we indeed obtain an isotropic dielectric function

$$\epsilon_e = \epsilon_h + 3f\epsilon_h \frac{(\epsilon_{\perp} + 2\epsilon_h)(\epsilon_{\parallel} - \epsilon_h) - 2\epsilon_h(\epsilon_{\parallel} - \epsilon_{\perp})}{(1-f)(\epsilon_{\perp} + 2\epsilon_h)(\epsilon_{\parallel} + 2\epsilon_h) + f\epsilon_h(\epsilon_{\perp} + 2\epsilon_{\parallel} + 6\epsilon_h)}. \quad (6)$$

Equation (5) can be used to calculate $\tilde{\epsilon}_e$ for any appropriate orientation distribution of the inclusions. It is expected, however, that the results presented below for the metal–insulator transition remain qualitatively unchanged by such variations [11].

In the present model, we view the host ϵ_h itself as a macroscopically isotropic homogeneous system made up of the same anisotropic material as the inclusions. Roughly speaking, it may be taken as a polycrystalline collection of anisotropic, randomly oriented, compact grains much smaller than the spherical inclusions. Its dielectric properties can then be calculated from the principal elements of the local dielectric tensor ϵ_{\parallel} and ϵ_{\perp} using the well known effective medium approximation (EMA) [9, 13]

$$p \frac{\epsilon_{\parallel} - \epsilon_h}{\epsilon_{\parallel} + 2\epsilon_h} + (1-p) \frac{\epsilon_{\perp} - \epsilon_h}{\epsilon_{\perp} + 2\epsilon_h} = 0 \quad (7)$$

where p is the ‘effective’ volume fraction of ϵ_{\parallel} . Now in a mixture of two isotropic components, p would be the volume fraction of the component with dielectric constant ϵ_{\parallel} . In our model, however, the material is a collection of randomly oriented polymer chains, and the concept of a volume fraction has no clear definition. Instead it should be viewed as a measure of the connectivity of the component ϵ_{\parallel} . In highly disordered samples, the polymer chains are relatively short. This leads to short continuous paths of ϵ_{\parallel} , only a few of which will connect opposite sides of the entire system. This low connectivity corresponds to a small value of p . By contrast, in samples with lower disorder the polymer chains are longer, on average, and create more extended continuous paths of ϵ_{\parallel} . These samples will have relatively many paths of ϵ_{\parallel} which span the entire system, and therefore higher connectivity and a larger effective value of p .

The EMA of (7) is well known to predict a percolation transition at $p = p_c = 1/3$. It therefore provides a simple mechanism for a percolation induced insulator–metal transition in disordered polymers. Highly disordered systems will have effective values of p lower than p_c , and therefore lie below percolation. Systems with low disorder have higher connectivity values $p > p_c$ and therefore fall above the percolation threshold.

The bulk effective dielectric tensor of the entire system is now obtained by substituting the EMA result for ϵ_h into the MG approximation, equation (6). To illustrate the predicted dielectric behaviour for such a disordered system, we consider a highly simplified model of a quasi-one-dimensional conductor. In the high-conductivity direction we assume a Drude

metal with an additional term arising from bound charge carriers:

$$\epsilon_{\parallel}(\omega) = 1 - \frac{\omega_p^2}{\omega(\omega + i/\tau)} + \frac{\omega_s^2}{\omega_0^2 - \omega^2 - i\gamma\omega}. \quad (8)$$

Here the first two terms are the dielectric function of a simple Drude metal with plasma frequency ω_p and mean relaxation time τ . The third term represents an additional contribution arising from bound charge carriers within the ordered uniaxial inclusions, which are assumed to have a characteristic resonance frequency ω_0 . The amplitude ω_s and damping constant γ are material-dependent constants describing these bound charge carriers. We assume that the dielectric constant in the perpendicular directions is simply that of an insulator:

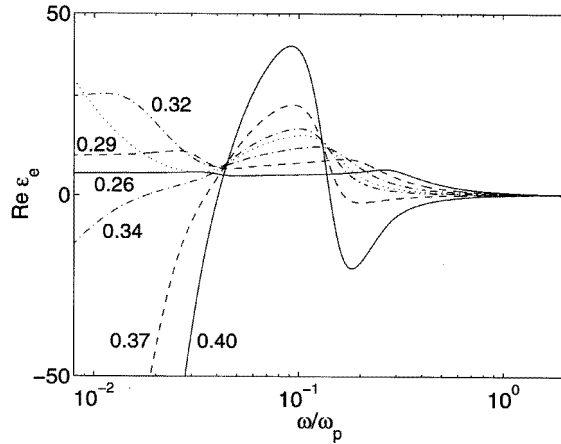
$$\epsilon_{\perp}(\omega) = 1. \quad (9)$$

Figure 2 shows typical results for this model, for samples with different values of the connectivity parameter p both below and above the percolation threshold. For the volume fraction of the inclusions we choose $f = 0.5$, a value which approximates the degree of crystallinity reported for highly conducting samples of doped polypyrrole [5]. Following the same experimental data, we choose $\omega_p\tau = 100$ for the metallic component ϵ_{\parallel} . The constants ω_0 , ω_s and γ , are not explicitly available from the data. Their normalized values, $(\omega_0/\omega_p)^2 = 0.02$, $(\omega_s/\omega_p)^2 = 10$ and $\gamma/\omega_p = 0.1$, were chosen as an example that produces a very good agreement with the experimental results of [6]. It is important to emphasize that changing these values does not change the main qualitative features of the metal–insulator transition as reported below.

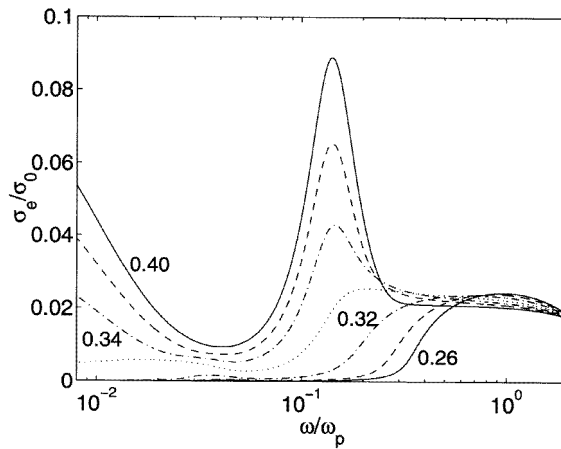
The effective dielectric function of figure 2 clearly shows a transition from dielectric to metallic behaviour of the dielectric coefficient, associated with an increase in the low-frequency electrical conductivity. The resulting frequency-dependent conductivity and dielectric coefficient exhibit all the important characteristics observed in the experiments. In low-connectivity systems ($p < 1/3$), the conductivity has a peak near the plasma frequency ω_p , which moves towards lower frequencies as p increases. In this regime of p , the conductivity decreases sharply to zero at low frequencies ($\omega < 0.1\omega_p$). The corresponding dielectric coefficients are positive and small over the entire range of frequencies. They increase more sharply with decreasing frequencies in samples with higher connectivities, and larger low-frequency conductivities. Precisely at the percolation threshold ($p = p_c = 1/3$), the low-frequency conductivity does not fall to zero but instead stays constant over a wide range of frequencies. The same behaviour is observed experimentally in polyaniline samples near the insulator–metal transition. The dielectric coefficient of this system (at $p = p_c$) increases sharply at low frequencies and is positive at all frequencies.

A qualitatively different behaviour is obtained in higher-connectivity systems, where $p > p_c$. In this case, the conductivity develops a stronger peak at intermediate frequencies ($\omega \approx 0.1\omega_p$). As p increases, this peak moves to lower frequencies. The conductivity increases again at very low frequencies ($\omega \approx 0.01\omega_p$), to values that are only slightly lower than the maxima near $\omega \approx 0.1\omega_p$. This low-frequency increase becomes more pronounced in samples with higher connectivities. Just such behaviour has been observed in polyaniline, in the sample with the highest d.c. conductivity [6].

The dielectric coefficients of these high-connectivity samples exhibit three zero crossings and two frequency bands of negative $\text{Re } \epsilon_e$. In the lower of these two bands ($\omega < 0.1\omega_p$), $\text{Re } \epsilon_e$ is large and negative, becoming more negative with increasing p . The second, and much shallower, band develops at intermediate frequencies. Both negative bands become



(a)



(b)

Figure 2. (a) The bulk effective dielectric coefficient $\text{Re } \epsilon_e(\omega)$, and (b) the electrical conductivity $\text{Re } \sigma_e(\omega)$ (normalized by $\sigma_0 = \omega_p^2 \tau / 4\pi$) for the model of figure 1. Results are shown for connectivities p above the percolation threshold: $p = 0.34$ (dash-dot line), $p = 0.37$ (dashed line), $p = 0.40$ (solid line); at the threshold (dotted line); and below it: $p = 0.26$ (solid line), $p = 0.29$ (dashed line), $p = 0.32$ (dash-dot line).

broader with increasing connectivity p . Between these two bands $\text{Re } \epsilon$ is positive and, for a given frequency, is a monotonically increasing function of p .

These results show that our macroscopically disordered structural model can easily reproduce the experimentally observed dielectric response of conducting polymers. The calculated $\text{Re } \epsilon_e(\omega)$ shows all the distinctive characteristics of the experimental results near an insulator–metal transition, and also depends in the same way on the d.c. conductivity. When the host is at or below percolation, $\text{Re } \epsilon_e(\omega)$ is positive at low frequencies, while for an above-percolation host, $\text{Re } \epsilon_e(\omega)$ is negative over a broad range of low frequencies, in good agreement with experiments on both polypyrrole and polyaniline [5, 6]. Furthermore, these results confirm, in agreement with experiment, that $\epsilon(\omega)$ should be strongly dependent on the microstructure of the polymer system. Finally, our composite results also exhibit a

characteristic peak in $\sigma_e(\omega)$. This peak, which extends down to very low frequencies, arises from localized oscillations of the charge carriers in one or a few crystallites of polymer; the carriers are localized because of the disordered microstructure (which is characterized by a spatially varying dielectric tensor). Such a peak is typical of the conducting polymers, where it has been attributed to both composite effects [5, 6, 14] and to Anderson localization [4]. The present results support the idea that this behaviour may be due simply to the inhomogeneity of the polymer medium, without the necessity of invoking Anderson localization.

In summary, we have described a simple model to treat macroscopic disorder in systems of quasi-one-dimensional organic conductors. The model combines a Maxwell–Garnett treatment of anisotropic inclusions with an effective medium approach for calculating the properties of the isotropic host. The model leads to a macroscopic dielectric behaviour which agrees with experiments on polypyrrole and polyaniline, and accounts for the dependence of $\epsilon_e(\omega)$ on the static electrical conductivity.

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