

Macromolecular disorder and electron localization: A numerical study with application to Se

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We present a numerical study of a simple model to describe the electronic structure of polymer fluids such as liquid Se. Using a simplified geometry and a one-electron tight-binding Hamiltonian, we investigate the density of states and the localized or extended nature of eigenstates. The metallic or nonmetallic character of the system is analyzed utilizing a scaling procedure. With increasing chain length, a transition from metallic to nonmetallic behavior can be observed, indicated by the presence of localized states in a pseudogap.

I. INTRODUCTION

Liquid selenium—a typical semiconductor at the melting point—shows a dramatically increasing conductivity when approaching the critical point ($p_c=380$ bars, $T_c=1860$ K).¹ The conductivity saturates at 1700 K, with values close to metallic conductivities ($100\text{--}300\ \Omega^{-1}\text{cm}^{-1}$), which strongly depend on the pressure. The properties of liquid Se, including this transition from a liquid semiconductor to a fluid metal have provoked a large amount of theoretical and experimental work.²

It is generally believed that this metal-nonmetal transition is induced by a change in the structure of *l*-Se. At the melting point, the highly viscous liquid consists of chains of $N=10^5\text{--}10^6$ atoms.³ The structure of *l*-Se under these conditions can be described by random chain models,⁴ with nearest-neighbor distances and bond angles similar to those in the crystalline solid, as indicated by neutron-scattering experiments.⁵ Recent first-principles molecular-dynamics studies of Se (Ref. 6) show a wide distribution of dihedral angles. The gradual loss of parallel chainlike configurations with increasing temperature has been interpreted in two different ways:⁵ either by the increase of small Se rings in a ring-chain equilibrium or by the shortening of the Se chains. Whereas the postulation of a ring-chain equilibrium seems to be of questionable relevance to the structural properties of *l*-Se,⁷ the shortening of the chains has been confirmed by a ⁷⁷Se NMR study of Warren and Dupree,⁸ with an average degree of polymerization decreasing from $N=750$ at 873 K to $N=7$ at 1823 K. X-ray scattering and optical absorption experiments also indicate a chain length of seven atoms at 1500 K and 510 bars.⁹ In the vicinity of the critical point, *l*-Se has been described as a molecular rather than a metallic fluid,¹⁰ with Se_2 molecules as the dominant species.¹¹

In this paper we introduce a simple model to study the influence of the length of polymer chains on the electronic structure and thus the metallic or insulating character of the model. The major purpose of this paper is to show that such a model leads to a metal-insulator transition and to give some new insights into the nature of this tran-

sition. Any detailed computation of the conductivity as a function of pressure, density, or temperature is out of reach due to the extreme simplifications introduced. In Sec. II, details of the model studied will be presented, including the generation of the geometry, the description of the electronic structure, and the way the metallic or nonmetallic character of eigenstates is deduced. In Sec. III, the results are presented and discussed. Conclusions are derived in Sec. IV.

II. THE MODEL

Crystalline Se can be represented on a cubic lattice, with a slight deformation of the bond angles to meet the experimental value.¹² We have set up a similar model for fluid Se: on a simple cubic lattice, short polymer chains of length N are created by a pseudo-random-walk procedure. Although in a real macromolecular fluid a distribution of chain lengths may be observed, all chains in the model show the same length. An ensemble of chains is created in the following way. For each chain i , we chose a site $\mathbf{r}_i^0=(x_i^0, y_i^0, z_i^0)$ to start the walk at random. If \mathbf{r}_i^0 is occupied, the procedure is repeated until an empty site is hit. For the second atom of chain i , one of the six neighbor sites of the first atoms is chosen at random. If this site \mathbf{r}_i^1 is occupied by an atom of another chain which has been built previously, the first atom of the chain is removed from the lattice and the procedure to generate chain i is restarted.

If \mathbf{r}_i^1 has been accepted as an atom of chain i and $N>2$, the following procedure is repeated for $n=1$ to $N-1$: out of the four neighbor sites of \mathbf{r}_i^n which give rise to an angle $\angle(\mathbf{r}_i^{n-1}, \mathbf{r}_i^n, \mathbf{r}_i^{n+1})=\pi/2$ one is chosen at random. If \mathbf{r}_i^{n+1} is occupied by another Se atom, then all atoms of chain i created so far are deleted and the generation of the chain is restarted. If \mathbf{r}_i^{n+1} was an empty site, the procedure is continued until $n+1=N$, so the chains are grown sequentially. The method is successful because of the low density of Se atoms per lattice site (see below) and the short chain lengths (up to $N=32$) which are studied. The spacing of lattice points is $2.38\ \text{\AA}$, due to the cubic structure all bond angles are equal to $\pi/2$. The dihedral

angles can take the value of zero, $\pi/2$, π , or $3\pi/2$. For the results presented in this work, a density of Se atoms per lattice point of $\frac{1}{2}$ has been chosen as a compromise between the reproduction of the correct density and the correct number of next-nearest neighbors at the melting point. This density is fixed for all chain lengths studied, requiring a continuous increase of pressure in a hypothetical experiment. As the dynamics of the system has been neglected, the model presented here can also be interpreted as an amorphous solid generated by quenching the liquid.

The electronic structure of the model is described by a nearest-neighbor tight-binding Hamiltonian:¹²

$$\hat{H}|i\rangle = \epsilon_i|i\rangle + \sum_{j \neq i} V_{ij}|j\rangle, \quad (1)$$

where the identification of neighbors refers to their position on the cubic lattice. The low-energy s orbitals are ignored by setting $\langle s_i|\hat{H}|p_j\rangle = 0$, the three remaining p orbital problems separate due to the symmetry of the underlying lattice. Without any loss of generality, the p orbital site energy ϵ_p can be set to zero. To describe the Hamiltonian, four interaction parameters are required: the intrachain matrix elements for σ and π interactions, $V_{pp\sigma}$ and $V_{pp\pi}$, and the same matrix elements for interchain interactions, which will be indicated by a tilde hereafter.

In this study, the ratios $V_{pp\sigma}/V_{pp\pi} = -4$, $V_{pp\sigma}/\tilde{V}_{pp\sigma} = 4$, and $\tilde{V}_{pp\sigma}/\tilde{V}_{pp\pi} = -4$ have been used. The sign of $V_{pp\sigma}$ is positive, the interaction between two neighbor atoms being bonding if the wave function shows no node between these atoms; and the opposite sign of the expansion coefficients of the wave function is observed on neighboring atoms. The sign of $V_{pp\pi}$ is negative. All energies are measured in units of $V_{pp\sigma}$, which is given by 4.36 eV in Harrison's $1/r^2$ parametrization.¹² This model naturally includes $C_1^0(D_0)$ centers at the end of the polymer chains and defects comparable to $C_3^0(D_3)$ centers whenever the end atom of a polymer chain is a neighbor of another twofold coordinated atom on another chain, or on the same chain, but more than two bonds away. As this is a one-electron model it cannot describe any kind of energy changes associated with the formation of charged defects.¹³

To decide about the metallic or nonmetallic character of a disordered system such as a fluid, it is not sufficient to look at the density of states alone to see whether the Fermi energy lies within a band or a band gap. Following Anderson,¹⁴ all the states within a band can be localized provided the disorder exceeds a critical value. Below the critical value of disorder, localized and extended states are separated by a mobility edge E_c .^{15,16} As charge transport between localized eigenstates requires phonon-assisted hopping, electron localization due to disorder has a dramatic influence on the temperature dependence and on the numerical value of the conductivity.

The localized or extended character of eigenstates is computed using the scaling method of Thouless, Edwards, and Licciardello, abbreviated TEL.¹⁷ These authors have shown that the dimensionless ratio of energies

$\Delta E/\delta E$ (the Thouless number) is proportional to the conductance g of the system. δE is the average spacing of energy levels and ΔE the shift of energy levels caused by a change in boundary conditions. ΔE is usually taken as the geometric mean within a certain energy interval. In this work, we use the weak-decoupling version of the TEL method.¹⁸ For a given energy and degree of disorder, i.e., density and chain length N , the Thouless number is computed as a function of system size L . Whenever the scaling function

$$\beta(L, E, N, \rho) = \frac{d \ln g(L, E, N, \rho)}{d \ln L} \quad (2)$$

is smaller than zero, the conductance is decreasing with increasing system size, and the corresponding eigenstates are localized. If $\beta(L)$ is larger than zero, the corresponding eigenstates are identified as extended ones. This interpretation of β follows the scaling theory of localization.¹⁹

III. RESULTS AND DISCUSSION

For the model described above, the electronic structure was computed for chain lengths of $N=2, 4, 8, 16$, and 32 . To apply the TEL method, system sizes of $L=10, 12, 14$, and 16 have been studied. 573 realizations have been investigated for the smallest system size, and 35 realizations have been performed for $L=16$. The resulting tight-binding matrices had a maximum dimension of 2048. As only eigenvalues had to be computed, a Lanczos algorithm has been used for the diagonalizations.²⁰

In Fig. 1, the density of states is shown for three

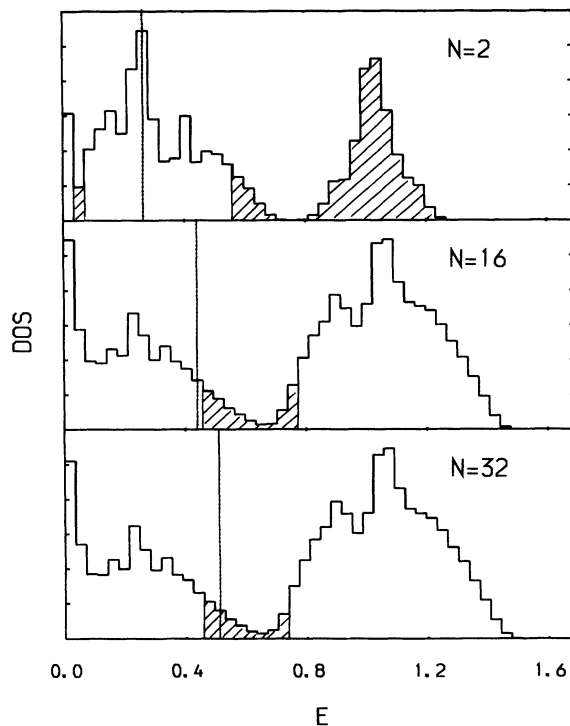


FIG. 1. The density of states (DOS) as a function of energy for polymer chain lengths $N=2, 16$, and 32 . Localized regions of the spectrum have been shaded, the Fermi energy is marked by a solid line. Energy in units of nearest neighbor hopping matrix elements $V_{pp\sigma}$, density of states in arbitrary units.

different degrees of polymerization. The simple cubic lattice is bipartite, so the density of states is symmetric about $E=0$. As expected, the general structure of the density of states can always be described by a band of $pp\sigma$ -nonbonding orbitals at low energies and a band of antibonding orbitals at high energies. For $N=2$, the smallest polymer studied, the antibonding band is very narrow compared to the nonbonding band. As each polymer chain has two pairs of nonbonding orbitals instead of one—as would be characteristic for the infinite chain—the ratio of eigenstates in the nonbonding band versus the weight of eigenstates in the bonding and in the antibonding band is 2:1. The nonbonding band has a considerable substructure, whereas the antibonding band is rather smooth. The bands are separated by a small band gap. The Fermi energy, indicated by a solid line, is located deep in the nonbonding band. For $N=16$, the width of the antibonding band has grown considerably, because a large number of states have been moved from the nonbonding to the antibonding band; a result of the decreasing number of C_1^0 centers. The band gap has disappeared and the density of states in the former gap is small but nonzero. The Fermi energy has been shifted towards the former band edge of the nonbonding band. Looking at the density of states at $N=32$, little difference can be observed compared to $N=16$; the width of the antibonding band has increased slightly, but the gross features are the same. Even the same density of states substructure can be found when comparing the $N=16$ to the $N=32$ case. The major difference is that the Fermi energy has been shifted further to a higher energy and a smaller density of states. As will be shown below, this shift of the Fermi energy becomes crucial when the question of the insulating or metallic character of the system arises.

As indicated above, for disordered systems the study of the localized or extended nature of eigenstates at E_F becomes essential in order to determine the metallic or nonmetallic (i.e., semiconducting or insulating) character of the system. In Fig. 2, the TEL analysis is presented for the same degrees of polymerization as given in Fig. 1. The entire spectrum has been divided into 48 intervals. Within each of these energy bars, the negative logarithm of the Thouless number is plotted as a function of system size, with L increasing from left to right. Whenever $g(L)$ is decreasing with increasing system size, the corresponding states are identified as being localized and the energy bar is labeled by an L. For $N=2$, the entire antibonding band exhibits a localized character. In addition, a large region of localized states exists at the upper band edge of the nonbonding band, and a small interval of localized states can be found close to the center of the nonbonding band. The Fermi energy, however, is well located in a region of extended states, thus indicating a metallic character of the system. Like the density of states, on a bipartite lattice the localization properties are symmetric about $E=0$. For $N=16$, a small interval of localized states can be observed in the region of a small density of states between the nonbonding and the antibonding band. This overlapping of localized band tails is identical to the Cohen-Fritzsche-Ovshinsky model of a pseudogap in

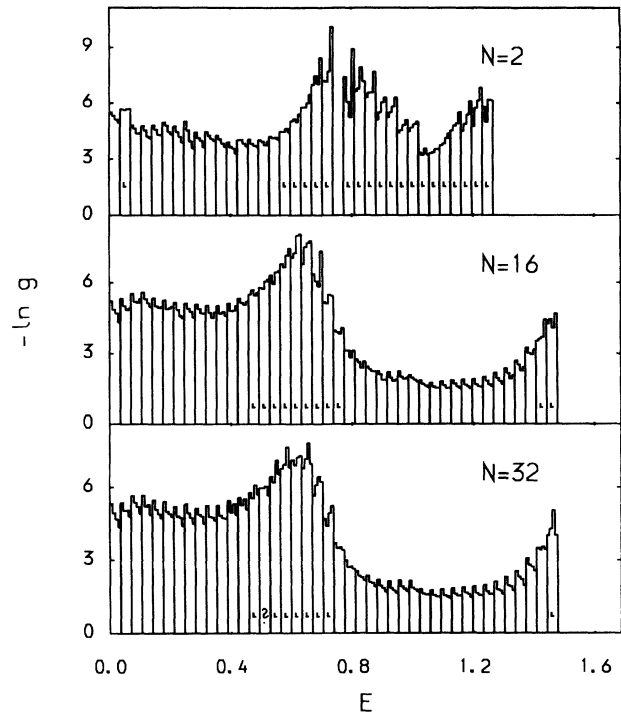


FIG. 2. The scaling analysis for polymer chains of length $N=2$, 16, and 32, deciding about the localized or extended nature of eigenstates. Scaling behavior of the negative logarithm of the dimensionless conductance as a function of energy. For details see text. Energy in units of nearest-neighbor hopping matrix elements $V_{pp\sigma}$.

amorphous semiconductors.¹⁵ The Fermi energy, considerably higher than for $N=2$, is still smaller than the energy of the mobility edge, so the $N=16$ system still shows a metallic character. The $N=4$ and $N=8$ systems—not shown here—smoothly interpolate between the density of states and the localization properties computed for $N=2$ and 16. For $N=32$, the TEL analysis becomes somewhat ambiguous close to the Fermi energy. Whereas the Fermi level lies in a small region of extended states, it is surrounded on both sides by localized states. The scaling behavior in some of these intervals is not monotonous. At best we can say that the Fermi edge and the mobility edge get close here, indicating the point of the metal-insulator transition or even the onset of the localized domain. The major difficulty in studying larger chain lengths is the fact that polymer chains carry along their own length scale $R_{rms} = \sqrt{N}$, which is comparable to the system size for $N=32$. In order to perform a high-quality scaling analysis close to the critical value of N , the smallest system size has to be at least $L = 2R_{rms}$, to rule out the influence of the correlation length of the chain.

As the density of particles in the system is close to the quantum percolation threshold $p_q \approx 0.44$,²¹ the location of the mobility edges and the localized and extended nature of eigenstates is sensitive to a reduction of the density. On the other hand, an increase of the effective number of neighbors or the interchain coupling strength rap-

idly delocalizes eigenstates and closes the band gap between the nonbonding and the antibonding band. Therefore, the critical value of N at which a metal-nonmetal transition occurs can easily be altered by a change of the parameters of the model.

In the region close to the metal-nonmetal transition, the density of states and localization properties computed in this work confirm the picture derived by Warren and Dupree⁸ to describe the transition. An Anderson transition is induced by the structural change of the fluid, and C_1^0 centers play a dominant role. As larger chain lengths cannot be studied without greatly enlarging the system size, we are unable to test whether a well-separated and strongly peaked impurity band exists in the regime of long polymer chains. For values of N up to 32, we find no evidence for the splitting of the impurity band and the nonbonding band.

IV. CONCLUSIONS

Motivated by the strong increase of the conductivity of fluid Se with increasing temperature and pressure, accompanied by a drastic change in the degree of polymerization, we have introduced a simple model to study the influence of the length of Se_N chains on the electronic structure of the system.

The geometry of the system has been modeled by short self-avoiding random walks of length N on a simple cubic lattice. The electronic structure of the model is described by a nearest-neighbor tight-binding Hamiltonian involving only p orbitals, with both intrachain and interchain interactions taken into account. The interchain interactions lead to an effective coordination number larger than two, but charged defects are not taken into account. To resolve the localized or extended nature of the eigenstates—and therefore their metallic or insulating character—the scaling behavior of the conductance is studied.

With increasing chain length N , the Fermi energy gradually moves from a region of extended states within the nonbonding p band into a pseudogap of localized states between the nonbonding and the antibonding p bands. In the region close to the metal-nonmetal transition the density of states and the localization properties

computed here confirm the picture derived by Warren and Dupree⁸ to describe the transition. An Anderson transition is induced by the structural change of the fluid, and C_1^0 centers play a crucial role.

Whereas we have been able to show that a simplified model of both the geometry and the electronic structure leads to an Anderson-like metal-insulator transition in a disordered polymer fluid, this model has to be upgraded in many ways to meet the final challenge of all computer simulations, the comparison with experiments. *Ab initio* molecular-dynamics studies⁶ or potentials fitted to produce comparable results may turn out to be valuable to obtain better geometric models. In a more advanced study, both hybridization effects and the presence of charged defects should be included.

The simple model represented in this article leads to a uniform distribution with equal probability of finding a dihedral angle ϕ of zero, $\pi/2$, π , or $3\pi/2$. The dihedral angle affects the sequence of $V_{pp\sigma}$ and $V_{pp\pi}$ hopping matrix elements such that whenever any nonuniform distribution $p(\phi)$ is generated, correlation is introduced into that sequence. The *ab initio* density-functional simulations of Hohl and Jones⁶ show a $p(\phi)$ peaked around $\pm\pi/2$ both at high and low temperatures, similar to that observed in a crystal. In the model presented here, a random sequence of two dihedral angles $\pm\pi/2$ would have lead to a periodic sequence $V_{pp\sigma} - V_{pp\pi} - V_{pp\pi}$ and thus to a perfectly ordered system, provided the interchain coupling is neglected. Once interchain coupling is recovered and each polymer chain shows a periodic sequence of hopping matrix elements, the disorder present in the system is reduced compared to a system showing a random sequence of dihedral angles. Thus, localization is expected to be suppressed.

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