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Computationally characterizing charge transport resiliency in molecular solids: Electronic Supplementary Information

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1 Constructing a weighted graph from MD data

In order to constructed a directed, weighted graph from the nodal representation of monomers in MD system, we require to define (a) neighborhood/connectivity and (b) probability/ease of hop across that edge. Neighborhood is defined with respect to the average electronic cloud around the monomer, represented through a bounding ellipsoid around the atoms. The size of the bounding ellipsoid is closely related to the average radius of the electronic cloud around the monomer. Monomers with overlapping electronic cloud are deemed adjacent for the construction of the graph, i.e., we equivalently assign an edge in MDGraph. Next, all adjacent monomers are not equally likely to conduct a charge. Thus, each edge is assigned a particular weight, higher weights denoting higher difficulty to conduct charges while lower weights denote ease of charge transport. As a reference edge weight, we choose the edge weight between two consecutive planar monomers along the direction of the electric field to be equal to $w_0 = 1$. We then distinguish every other edge with respect to this reference edge and assign proper weights as follows:

1. **Type of connection:** The first distinction between the edges we make is whether adjacent monomers belong to the same chain or to different chains. Intuitively, charges prefer to travel along the chain than to jump across chains. So, we assign a higher weight (an inter-chain factor) to edges that connect monomers across different chains, $w_{ic} = 100$.

2. **Transfer Integral / electronic coupling between the monomers:** Monomers that have perfect overlap of π-orbitals have the highest charge hop probability. The coupling in intrachain edges are predominantly effected by the relative orientation of the two monomers (since their relative locations are fixed). Adjacent monomers that are planar will have the highest coupling while those which are relatively perpendicular to each other will have zero coupling. This weight, represented by $\mathbf{w_{ti}}$ is a function of the relative orientation, and ensures that perfectly aligned have a weight of $w_{ti} = 1$ and perfectly perpendicular monomers have a large weight $w_{ti} = 1000$. In this work, we assume a sinusoidal variation of the transfer integral with the relative orientation between the close monomers.

   The transfer integral between inter-chain monomers is determined by several factors. In this work, we mainly focus on three factors of transfer integral: (i) distance between the monomers, (ii) slip between the monomers and (iii) relative orientation between the monomers. Based on previous work[1], we chose a near exponential decay of the coupling with distance between monomers. In other words, we chose a weight factor $\mathbf{w_{ti_1}} \propto \exp(\alpha_1 \mathbf{d})$ to model the effect of distance on the edge weight. As described in the same work, we chose a exponentially decaying sinusoidal function to model the effect of slip on the transfer integral: $\mathbf{w_{ti_2}} \propto \exp(\alpha_2 \mathbf{d_{slip}}) * \mathbf{sin}(\alpha_3 \mathbf{d_{slip}})$. The relative orientation across the chains is treated the same way as in the case of intra-chain monomers.

3. **Effect of electric field:** Electric field determines the predominant direction of charge transport. In other words, charges prefer to flow along the field than against the field. We assign a extra weight to represent that difficulty of charges to traverse against electric field: w_{ef}. This is chosen such that weight is low for edges along the electric field and high against the electric field.

Finally, we calculate the total weight of an edge by multiplying all these factors together:

$$w_{total} = w_0 \times w_{ic} \times (w_{ti} \times w_{ti_1} \times w_{ti_2}) \times w_{ef}$$

1.1 Assigning electrodes

Having constructed a graph, we need to assign a start and end nodes for charge initiation and termination respectively. In an OE device, these would be the electrodes. Since the MD simulation is not grown between physical electrodes, we choose a particular fraction of the total length as the respective electrodes. Specifically, in this work, for each direction, we chose monomers in the first 1% length to be connected to the source electrode and those monomers in the last 1% length to be connected to the destination electrode. This is based on an underlying assumption that all these nodes/monomers are equally likely to carry a charge from/to the source/destination electrode. Equivalently on a graph, we connect all these nodes to a meta-node representing an electrode. Any edge emanating from an electrode is given a very low weight, or equivalently, a very high probability of a charge choosing the edge.

1.2 Analysis of centrality metrics

One question remains about which network centrality measure captures the charge transport phenomena most accurately. To this end, we repeated the above presented study with several commonly used centrality measures, namely closeness centrality, degree centrality, betweenness centrality and eigenvector centrality. The results, similar to **??** are presented in fig. 1.

As can be seen in fig. 1, both degree and closeness centrality did not give very meaningful results, primarily because the concepts defining them are unaligned with the concepts underlying physics of charge transport between electrodes

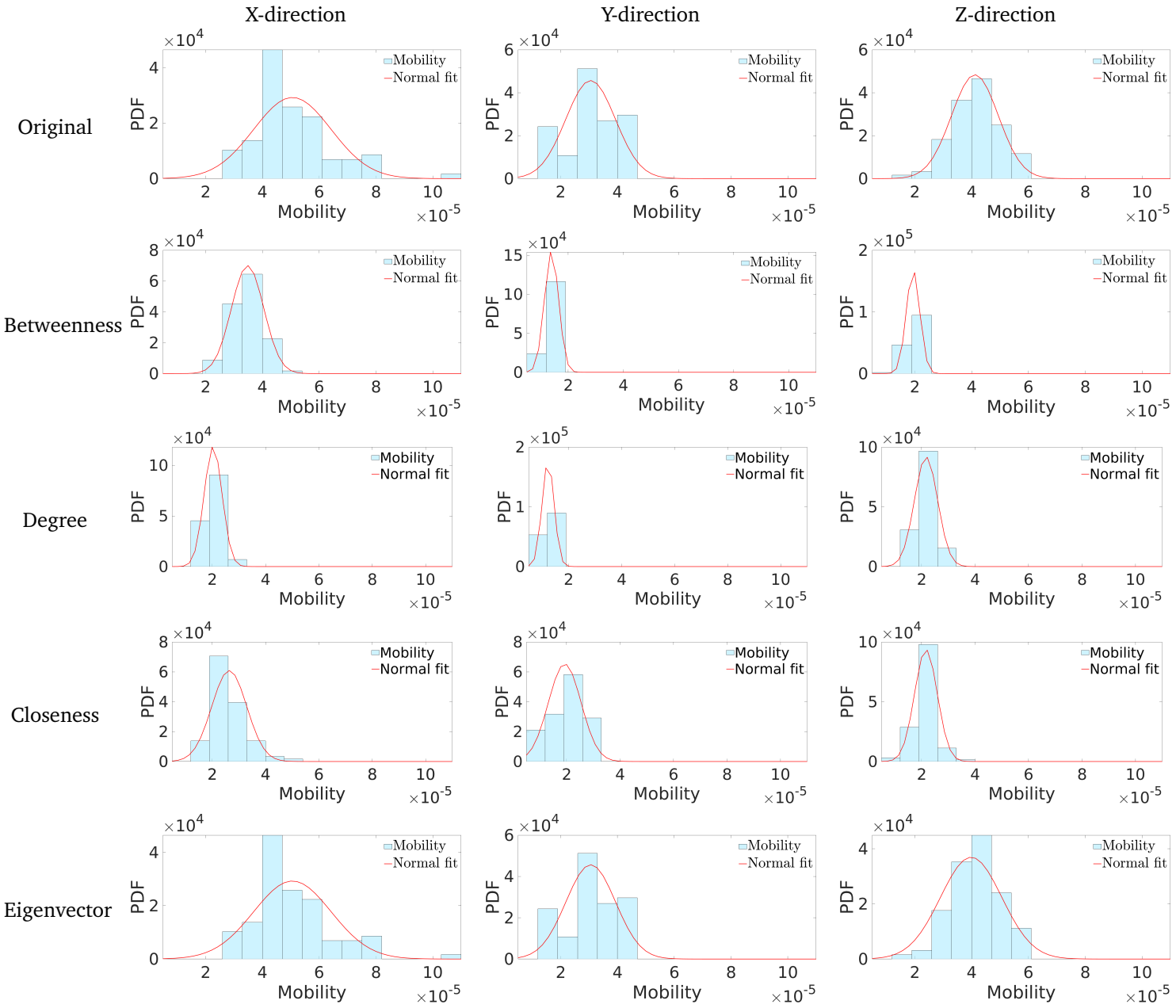

Figure 1 Effectiveness of choice of centrality measure. The first rows shows the original mobility distribution of the molecular system, and the following rows depict the reduced mobility top 500 monomers are disabled between electrodes. Depending on the choice of the centrality measure, we remove the top 500 monomers identified with the highest centrality value.

(what we call algorithmic alignment). Finally, eigenvector centrality also was not as informative as betweenness centrality at predicting effect on charge transport. On further introspection, we realized that eigenvector centrality is correlated with degree centrality, which also might explain the low effectiveness of the metric to predict impact of defects/degradation on overall charge transport[2].

References

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