# Supporting Information Influence of Vapor Deposition on Structural and Charge Transport Properties of Ethylbenzene Films

Lucas W. Antony,<sup>†</sup> Nicholas E. Jackson,<sup>†,‡</sup> Ivan Lyubimov,<sup>†</sup> Venkatram Vishwanath,<sup>¶</sup> Mark D. Ediger,<sup>§</sup> and Juan J. de Pablo<sup>\*,†,‡</sup>

†Institute for Molecular Engineering, University of Chicago, Chicago, IL 60637, USA
‡The Institute for Molecular Engineering, Argonne National Laboratory, Lemont, IL 06349
USA

¶Advanced Leadership Computing Facility, Argonne National Laboratory, Lemont, IL 06349 USA

§Department of Chemistry, University of Wisconsin-Madison, Madison, WI 53706, USA

E-mail: depablo@uchicago.edu

#### Effective $T_{g}$

Three different cooling rates were applied to the system and the corresponding fictive temperatures calculated are presented in SI-Fig. 1. There is a slight effect observed for the faster cooling rates on the instantaneous density and Debye-Waller factor, which may suggest that higher rates are becoming less physical. As the thermostat decreases the temperature of the system, the system lags slightly behind in equilibration due to the timescale. To correct for this effect, snapshots are taken at various temperatures during the cooling process and allowed to equilibrate at the appropriate temperature for 1 nanosecond. The values reported are averaged over the nanosecond trajectories for five samples with the standard deviation given as the error bars.



Figure 1: Three different cooling rates were investigated: 1 K/ns (black), 5 K/ns (red), and 10 K/ns (blue). The temperature at which the intensive potential energy per particle deviates from the super-cooled liquid line (dashed cyan line) was used to estimate the  $T_{\rm f}$ , panel (c), which is estimated from the intersection of the glass line for  $q_{\rm c} = 1$  K/ns (dashed grey line) to be 146 K. The panels (a) and (b) display the temperature dependence of the middle bulk density,  $\rho_{\rm bulk}$ , and the average bulk Debye-Waller factor, respectively, with 146 K marked by a grey line.

#### **Rotational Relaxation**

A relaxation time  $\tau_{\rm rot}$  was extracted by fitting a stretched exponential to the rotational autocorrelation function with respect to the molecular orientation vector (SI-Fig. 2). The  $\tau_{\rm rot}$  and  $\beta$  for each fit are provided in SI-Table 1.



Figure 2: Angular correlation with respect to the molecular orientation vector described in Figure 1a averaged over the bulk region of the film. Each dotted solid line is a liquid or super-cooled liquid ranging in temperatures from 350 K down to 150 K, which is just 4 K above the effective  $T_{\rm g}$ . The dashed lines are fitted stretched exponentials to each decay curve.

Using the above parameters, a VFT fit was applied to extrapolate to the conventional glass transition temperature and to calculate the fragility.

Table 1: Parameters for stretched exponentials :  $C(\theta) = \exp\left(-\left(\frac{t}{\tau_{\text{rot}}}\right)^{\beta}\right)$ 

$T(\mathbf{K})$	$ au_{\mathrm{rot}}$ (s)	$\beta$
150	$3.68 \times 10^{-7}$	0.77
160	$2.66 \times 10^{-8}$	0.80
170	$4.78 \times 10^{-9}$	0.81
180	$1.19 \times 10^{-9}$	0.83
186	$6.74 \times 10^{-10}$	0.83
200	$2.34 \times 10^{-10}$	0.85
225	$6.99 \times 10^{-11}$	0.89
250	$3.39 \times 10^{-11}$	0.90
300	$1.37 \times 10^{-11}$	0.90
350	$7.84 \times 10^{-12}$	0.91



Figure 3: The VFT equation was fitted to  $\tau_{\rm rot}$  (red points) calculated for temperatures ranging from 150 K up to 350 K. Extrapolating this function to  $\tau_{\rm rot} = 100$  sec gives a conventionally defined  $T_{\rm g}$  of 128K for this model.

#### Substrate Temperature Comparison

The onset temperature calculated for the various vapor-deposited glasses are very similar, SI-Fig. 4. The films with a  $T_{\rm s}$  of 120K or 115K have a  $T_{\rm on}$  of approximately 173K and the films with a  $T_{\rm s}$  of : 105, 125, 130, 135, or 140K have a  $T_{\rm on}$  around 170K. Whereas, the slowest cooled glass with  $q_{\rm c} = 1$ K/ns, has  $T_{\rm on}$  of  $\approx 159$ K. Thus, all VD glasses have enhanced kinetic stability relative to the conventional glasses. This similar  $T_{\rm on}$  for the various  $T_{\rm s}$  is in agreement with how similar the inherit structure energies and the densities in SI-Fig. 4b are.



Figure 4: The liquid-cooled film with  $q_c = 1$  K/ns (black) and the vapor deposited films (colored) were subjected to a heating run at a rate of 5K/ns, after first being cooled to 90K for comparison. The average bulk Debye-Waller factor,  $\rho_{\text{bulk}}$ , and the intensive potential energy were calculated as a function of temperature (panels (a), (b), and (c) respectively). The onset temperature seems to be similar for all vapor deposited films except for  $T_s = 140$  K (dark cyan), but all are higher than the liquid-cooled glass.



Figure 5: The bulk density,  $\rho_{\text{bulk}}$ , is given as a function of cooling rate. The black points are calculated from the liquid-cooled glasses as a function of cooling rate,  $q_c$ . The vapor deposited glasses (colored points) are plotted by the predicted  $q_c$ , assuming a linear relation between  $\rho_{\text{bulk}}$  and the order of  $q_c$  (dashed line). Error bars are calculated from the standard deviation of three samples for vapor deposited films and five samples for the liquid-cooled.

#### Arrest Depths

The arrest times,  $t_a$ , and the depth at which it occurs,  $z_a$ , appear to have an exponential dependence on substrate temperature. There is a temperature regime where it appears linear, but the films at the lowest temperatures plateau as they approach 0 and the higher temperature films quickly increase as the films approach the simulated  $T_{\rm g}$ .



Figure 6: The distance from the surface that corresponds to the time of rotational arrest,  $z_a$ , as a function of  $T_s$ . An exponential function was fitted to the data (grey dashed lines).

#### **Bulk Films Molecular Orientation**

SI-Figure 7 provides the full  $\cos(\alpha)$  distribution for the liquid-cooled glass and a larger subset of the PVD glasses than provided in the main text. For reference, a dotted line is shown to illustrate the uniform distribution that is expected for a completely isotropic film.



Figure 7: Distribution of  $P_1 = \cos(\alpha)$  values in the bulk of the liquid-cooled glass (black), where  $q_c = 1$ K/ns, and vapor deposited glasses (colored). Calculated using a Gaussian kernel density estimation (bandwidth = 0.10).

#### Molecular Orientation and Distance Correlation

The probability of benzene ring alignment was calculated as a function of center of geometry (COG) distance. Averaging over molecules within the bulk region of the film, only neighbors that were within a cylinder of radius 1 nm centered at the COG of the benzene ring of interest and aligned with that normal of the benzene ring of that molecule were considered. Each column is normalized to one, giving the probability of a neighboring benzene ring having that cosine alignment for a given distance.

The distance from the center of the cylinder was calculated as follows. First, project the COG vector,  $v_{COG}$ , onto the benzene ring unit vector,  $v_{benz}$ , which is simply  $v_{projCOG} = (v_{COG} \cdot v_{benz})$ . The radial distance from the center of the cylinder is the magnitude of the vector  $v_{rad} = v_{COG} - v_{projCOG}$ .



Figure 8: The probability of absolute value cosine alignment of the benzene ring normals for neighbors at a give center of geometry (COG) distance, where each neighbor is within a cylinder of radius 1 nm centered on the benzene ring and pointing in the direction normal of the benzene ring.

## A Graph Theoretical Approach to the Orientational Correlation Networks

To further explore the distance dependence of orientational correlations we used a modification of a graph theoretic approach to charge transport networks developed in previous works. Using the absolute value of the dot-product of the pi-system unit normal vectors between two neighboring ethylbenzene molecules, we set up an adjacency matrix to describe the orientational connectivity of the ethylbenzene molecules within the middle section of the film. This adjacency matrix is defined as:

$$A_{ij} = \begin{cases} \operatorname{abs}(\boldsymbol{v}_{benz,1} \cdot \boldsymbol{v}_{benz,2}) & i \neq j \\ 0 & i = j \end{cases}$$
(1)

We can then form the Laplacian matrix using the strength matrix, S, and the adjacency matrix, A, by L = S - A. The second eigenvalue of this Laplacian matrix is known as the algebraic connectivity, and represents how well-connected the overall graph is.

We then compare the values of the algebraic connectivity for the liquid-cooled and 120K PVD films, obtaining values of  $0.0215 \pm -0.019$  for the latter, and  $0.0172 \pm -0.016$  for the former. While the PVD film shows a slight increase in the algebraic connectivity of the orientational correlation network relative to the liquid-cooled films, this result is well within the error bars, and thus by this metric the orientational differences in these systems manifest by the vector normal to ethylbenzene's pi-electron system are quite subtle, in agreement, with the previous section on molecular orientations and distance correlations.

### Charge Transport in Liquid Cooled



Figure 9: Histograms of the (a) molecular site-energies in eV and (b) the transfer integrals (eV) for the liquid-cooled glass.

#### **Bulk Region**

To define the bulk region for analysis, effects from both interfaces needed to be avoided as much as possible. The Debye-Waller Factor was considered for the change in mobility caused at each (arrested near the substrate, and higher mobility at the vacuum interface), as well as the density.



Figure 10: The Debye-Waller factor (dashed lines) and density (solid lines) as a function of z, where the substrate oscillates around 1 nm, for  $T_{\rm s} = 130$  K ( $0.89T_{\rm g}$ ). There are three independent samples (different colors) per substrate temperature. The bulk region is defined as z between 4.8 nm and 7.2 nm, where the surface effects from the substrate and the free-surface are dampened out.

Snapshot with the bulk region highlighted



Figure 11: (a) Image of the all-atom ethylbenzene model. The vector normal to the substrate,  $n_z$ , and the angle,  $\alpha$ , between it and the vector used to describe the molecular orientation. (b) Snapshot from the vapor deposition process. The particles that form the substrate are represented as a surface, the box edges are blue. Two newly inserted molecules are highlighted as red whereas the previously deposited molecules are colored by atom (cyan for carbon, white for hydrogen). The inner bulk region of the film used is colored with a darker blue.