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

Lucas W. Antony, Nicholas E. Jackson, Ivan Lyubimov, Venkatram Vishwanath, Mark D. Ediger, and Juan J. de Pablo

Supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, under Award DE-SC0012048.

ABSTRACT: Organic glass films formed by physical vapor deposition exhibit enhanced stability relative to those formed by conventional liquid cooling and aging techniques. Recently, experimental and computational evidence has emerged indicating that the average molecular orientation can be tuned by controlling the substrate temperature at which these “stable glasses” are grown. In this work, we present a comprehensive all-atom simulation study of ethylbenzene, a canonical stable-glass former, using a computational film formation procedure that closely mimics the vapor deposition process. Atomistic studies of experimentally formed vapor-deposited glasses have not been performed before, and this study therefore begins by verifying that the model and method utilized here reproduces key structural features observed experimentally. Having established agreement between several simulated and experimental macroscopic observables, simulations are used to examine the substrate temperature dependence of molecular orientation. The results indicate that ethylbenzene glasses are anisotropic, depending upon substrate temperature, and that this dependence can be understood from the orientation present at the surface of the equilibrium liquid. By treating ethylbenzene as a simple model for molecular semiconducting materials, a quantum-chemical analysis is then used to show that the vapor-deposited films exhibit increased energetic disorder and charge transport. The results suggest a novel structure–function simulation strategy capable of tuning the electronic properties of organic semiconducting glasses prior to experimental deposition, which could have considerable potential for organic electronic materials design.

INTRODUCTION

Glasses are typically formed by cooling a liquid at a sufficiently fast rate to avoid crystallization. As the liquid approaches the glass transition temperature, \( T_g \), the characteristic relaxation times and viscosity increase substantially, and eventually the supercooled liquid falls out of equilibrium. The properties of the resulting glass, such as its kinetic stability and density, depend on the cooling rate. Such properties can evolve over time by letting the material relax toward equilibrium, a process referred to as “physical aging”. Physical vapor deposition (PVD), a process in which molecules are deposited onto a substrate held at a temperature below \( T_g \), has been shown to create glass films with enhanced kinetic stability. For some materials, the properties of PVD glasses are in fact comparable to those expected of highly aged, liquid-cooled glasses.\(^1\) This enhanced stability has been observed for a variety of organic molecules, including indomethacin,\(^1\) several alkylbenzenes,\(^7\) toluene and ethylbenzene,\(^8\) several tris-naphthylbenzene (TNB) isomers,\(^15\) and several organic semiconductors.\(^17\) In recent years, the discovery of these highly stable glasses has motivated simulation efforts to create stable glasses in silico. Using a protocol based on the vapor deposition process, a series of simulation studies have examined the increased stability of vapor-deposited glasses relative to conventional glasses, and the influence of the process itself. That work has focused on relatively simple models that are known to be good glass formers. These include the so-called Kob–Andersen model,\(^18\)\(^–\)\(^20\) short-chain coarse-grained polymers,\(^21\) and a 2D version of the Kob–Andersen model.\(^22\)

Experimental studies have shown that the vapor deposition process can in some cases influence the average molecular orientation within the glass, leading to formation of anisotropic films.\(^23\)\(^–\)\(^24\) In particular, Yokoyama and others have demonstrated for several different semiconducting molecules that PVD films have a degree of anisotropic orientation that depends on...
molecular shape and deposition conditions, and that this anisotropic ordering can improve the charge carrier transport properties relative to isotropic films. Simulations of vapor deposition of short polymeric molecules have also shown that physical vapor deposition leads to stable anisotropic glasses. More recent studies of organic semiconducting PVD glasses and intraconazole, a smectic liquid crystal, have shown that the average molecular orientation can be systematically tuned as a function of the substrate temperature, \( T_s \), while retaining the enhanced density and kinetic stability that is imparted by the PVD process. The anisotropic ordering within the glass films is now thought to arise from the interfacial ordering that arises at the vacuum–liquid interface; that order is trapped in the glassy film as it is grown by PVD, leading to materials whose structure in the glass is different from that obtained in the bulk of liquid cooled glasses. The degree of structural ordering observed in PVD glasses is currently thought to be a feature of the vapor deposition process, but not necessary for enhanced stability. For instance, vapor-deposited glasses of tetrachloromethane, which is a mostly spherical molecule, form stable glasses (with high onset temperatures relative to the liquid-cooled material) and are expected to form isotropic glasses. Similarly, simulated vapor-deposited glasses of spherical particles exhibit significant kinetic stability and do not show any signs of ordering beyond those observed in liquid-cooled glasses.

Molecular simulations have provided important insights into the structure and properties of vapor-deposited glasses and into key features of the PVD process itself. However, all simulation studies to date have focused on simplified models that do not exhibit the structural richness of realistic, atomistic systems. An exception is provided by an early study of trehalose, which revealed significant anisotropy in a stable glass. Trehalose, however, has not been considered in experimental PVD processes, partly because it can easily crystallize, and it is therefore difficult to interpret the results of that study. In this work, we investigate the formation of glasses by physical vapor deposition for ethylbenzene (EB), and we examine its effects on molecular orientation and, importantly, on the corresponding charge transport descriptors that would be relevant for semiconducting applications. Ethylbenzene is one of the smallest PVD stable glass formers that have been studied in the literature. Carefully generated experimental data for this molecule are now available from multiple research groups, making it a good candidate for an in-depth computational study of an atomistic vapor-deposited glass. Note, however, that structural studies have not been performed previously on vapor-deposited films of ethylbenzene; it is therefore not known whether the resulting materials are isotropic or not. Our simulations provide evidence suggesting that the vapor deposition process can in fact be used to tune molecular orientation even in slightly asymmetric molecules, such as ethylbenzene. Along with those findings, we also examine the corresponding effect that PVD growth can have on the charge-transport properties of the resulting glassy films.

It is important to note that ethylbenzene itself is not a practically useful semiconducting molecule. However, from a theoretical point of view, it serves as an excellent model system for examining the impact of variable morphologies on relevant charge transport parameters; ethylbenzene’s conjugated ring and small alkyl side chain can be treated as a minimal model for the design motifs of common molecular semiconductors. Given the promise of vapor deposition to form stable glasses of organic semiconducting molecules, it is important to understand the impact that subtle changes in morphology may have on molecular-scale descriptors of charge transport. Since the majority of noncrystalline molecular semiconductors operate in the activated hopping regime of charge transport, which can be accurately described by a nonadiabatic theoretical framework, the two relevant parameters that are most strongly influenced by morphology are the molecular site energies and transfer integrals between molecules. The local site energy of a molecule, determined by the orientation of nearest-neighbor molecular dipoles, impacts the density of states through which charge transport occurs. If this density of states is too broad, due to large site-energy disorder, charge transport is inhibited by localization into low-energy trap states. Similarly, the transfer integral (electronic coupling) between the valence orbitals of two neighboring molecules dictates the maximum rate of charge hopping between those molecules; if the mean alignment of neighboring molecules results in poor molecular orbital overlap, the maximum possible rate of charge hopping decreases, and charge transport is hindered. While it is heuristically known that one can strongly influence these parameters via changes in morphology, a rational and systematic modification of these parameters via deliberate changes in processing parameters is difficult to achieve. Here we couple the ability to control orientational order in molecular simulations with a quantum-mechanical analysis of site energies and transfer integrals to understand the impact of PVD on charge transport parameters of stable glasses.

**RESULTS AND DISCUSSION**

Experimental observation time scales for glass behavior are typically on the order of seconds or longer, whereas for all-atom simulations, the accessible time scales are on the order of nanoseconds. Due to this discrepancy in time scales and rate dependence of glass properties, in simulations it is better to base the substrate temperatures for vapor deposition on the lowest practical simulated fictive temperature \( T_f \) rather than the conventional \( T_g \) for the material. The fictive temperature is given by the intersection of the equilibrium liquid property of interest (e.g., enthalpy or density) extrapolated to lower temperatures, and the glass property extrapolated to higher temperatures. A total of three cooling rates were considered here, namely: 10 K/ns, 5 K/ns, and 1 K/ns. The intensive per atom potential energy \( U_{atom} \) was used to define \( T_f \) as it exhibits a linear temperature dependence for both the glassy and liquid states. The change in slope when the liquid falls out of equilibrium is subtle; Supporting Information (SI) Figure 1c displays the temperature range over which the transition occurs. A dependence of about 6 K per decade decrease is observed in \( T_f \) as the rate is decreased for the three rates considered. The effective glass transition temperature \( T_g \) in this study is defined as the \( T_f \) for the slowest cooling rate, which is 146 K (marked by gray lines in SI Figure 1). The density, \( \rho_{bulk} \), and the average Debye–Waller factor for the middle bulk region (defined in Methods) are shown in panels a and b, respectively, in SI Figure 1. Classification is also observed in these two properties, where the rate of change is considerably slower once the material becomes glassy on the time scale of our simulations for both. The supercooled liquid deviates from the equilibrium line at higher temperatures as the rate increases, and becomes trapped in a lower-density and higher-energy state.

In order to validate the model, the conventional \( T_g \) value can be estimated via extrapolation. Conventionally, the glass
transition is defined as the temperature at which the structural relaxation reaches $t_\text{r} = 100$ s. Within the domain of $10^{-14} < \tau < 10^5$ and $T > T_g$, the relaxation times $\tau$ and the viscosity $\eta$ follow a Vogel–Fulcher–Tammann (VFT) expression of the form

$$\log(\tau) = A + \frac{B}{T - T_0}$$

(1)

SI Figure 2 shows the rotational autocorrelation for the bulk region of the films in the temperature range from 150 K up to 350 K. The VFT expression requires that the liquid films be fully relaxed, and, as evident in SI Figure 2, 150 K is the lower limit accessible to simulations. A stretched exponential was fitted to each rotational autocorrelation function, leading to a relaxation time $\tau_{\text{rot}}$ (the fit parameters are given in SI Table 1). The $\tau_{\text{rot}}$ relaxation times were fitted to the VFT relation (SI Figure 3), giving $A = -11.98$, $B = 206.8$ K, and $T_0 = 112.8$ K. Extrapolation of the relaxation times to $\tau_{\text{rot}} = 100$ s yields a $T_g \approx 128$ K. This value is not too different from the reported glass transition temperature for ethylbenzene of 115 K.\(^8,10,11\)

The fragility of the material can also be determined from the fit parameters according to

$$\log(\tau) = A + \frac{B}{T - T_0}$$

which gives a value of $m = 121$ by extrapolation. These values are in reasonable agreement with those calculated by Chen et al. in ref 10, who measured the dielectric relaxation of EB. In their results, a fit of $A = -15.0$, $B = 344.4$ K, and $T_0 = 95.5$, and $m = 97.5$ was obtained. Moreover, Chen et al. observed that the temperature dependence of the dynamics does not follow a single VFT law over the entire range of temperatures, such that temperatures closer to experimentally defined $T_g$ are not accessible to simulations, would lead to improved agreement. Note that $\tau_{\text{rot}}$ is already on the order of 100 ns at $T = 150$ K, which is comparatively the same order of magnitude as the longest practical runtime for all-atom films. The relaxation rate for films any lower in temperature would be far too large to equilibrate on practical time scales, which is in accordance with our lowest fictive temperature and effective $T_g$ of 146 K.

**Enhanced Stability.** Vapor-deposited films of ethylbenzene were generated according to the scheme outlined in Methods onto substrates with temperatures ranging from 95 K up to 145 K, which is just below the effective $T_g$ of our system (146 K). In order to assess the relative stability of the various films, the per atom inherent structure energy $E_{\text{IS}}$ was calculated for the bulk region of each film. The energy of the entire system was minimized after the film was cooled to 70 K at a rate of 10 K/ns, in order to allow the film to relax in the $x$ and $y$ dimensions prior to quenching. As illustrated in Figure 1, a linear fit to $E_{\text{IS}}$ relative to $\log(q_c)$ was used to extrapolate what the corresponding cooling rate would need to be in order to achieve the $E_{\text{IS}}$ of each vapor-deposited film. The $E_{\text{IS}}$ decreased approximately $7.7 \times 10^{-3}$ kcal/(mol-atom) per decade decrease in cooling rate. A similar calculation was performed on $\rho_{\text{bulk}}$ as discussed in the Supporting Information. Our results indicate that all the vapor-deposited films exhibit a lower $E_{\text{IS}}$ than the liquid-cooled glass. Note that PVD films are closely clustered together around an estimated cooling rate of 0.1 K/ns, which would take on the order of months to years of simulation time to produce by liquid cooling.

To further assess the relative stability of the films, we subjected them to a heating cycle at a rate of 5 K/qs. The temperature at which the film begins to return to the equilibrium liquid state, referred to as the onset temperature and denoted by $T_{\text{onset}}$, is a measure of kinetic stability. For the liquid-cooled glass, this $T_{\text{onset}}$ is $159$ K in Figure 2. All the PVD glasses prepared here have higher $T_{\text{onset}}$ with values in the vicinity of 170 to 172 K for all deposition temperatures considered here as seen in SI Figure 4. This finding is consistent with the enhanced $E_{\text{IS}}$ and $\rho_{\text{bulk}}$ observed for PVD films. For the sake of comparison, $T_s = 120$ K is the only PVD glass shown in Figure 2.

**Figure 1.** Intensive inherent structure energy, $E_{\text{IS}}$, for the bulk region. 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 $E_{\text{IS}}$ 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.

**Figure 2.** $T_{\text{onset}}$ comparison of the slowest cooled glass, $q_c = 1$ K/qs, and the films deposited at $T_s = 120$ K. The darker blue and the black curves represent the intensive potential energy of the film during a heating run at a rate of 5 K/qs. The films were then cooled and reheated at the same rate (light blue and dark cyan). The dashed lines are linear extrapolations from the glass line, and from the temperature range where the glass returns to an equilibrium supercooled liquid. Red and orange solid lines mark the onset temperature $T_{\text{onset}}$ for the liquid-cooled glass and vapor-deposited glass, respectively.
2. The PVD glass loses the enhanced stability upon entering the liquid state and has a $T_g$ of around 148 K upon cooling, as was observed previously for $q_s = 5$ K/ns.

**Structural Orientation.** The orientation of ethylbenzene molecules is quantified in terms of the vector pointing from the carbon atom para to the ethyl group to the $\alpha$-carbon of the ethyl group (SI Figure 11a). To characterize the molecular orientation within the bulk region of the films, we relied on two orientational order parameters defined by the first and second Legendre polynomials given by

$$P_1 = \langle n \cdot n_s \rangle_{\text{bulk}} = \langle \cos(\alpha) \rangle_{\text{bulk}}$$

$$P_2 = \langle P_1(n \cdot n_s) \rangle_{\text{bulk}} = \frac{3}{2} \langle \cos^2(\alpha) \rangle_{\text{bulk}} - \frac{1}{2}$$

where the dot product is between the unit vector along the molecular axis, $n$, and the unit normal to the substrate, $n_s$, as shown in SI Figure 11a. The dot product defines the cosine of the angle $\alpha$ between the molecular axis and $n_s$ and averaging was performed over all molecules within the middle bulk region of the film. The two order parameters provide complementary information about the average molecular orientation within the film. $P_1$ identifies if the molecules are pointed perpendicular to the substrate with the ethyl group pointed to the surface ($P_1 = 1$) or toward the substrate ($P_1 = -1$); however, a value of 0 can mean either that the film is isotropic or that molecules are parallel to the substrate. Parameter $P_2$ indicates if the molecule is generally perpendicular to the substrate ($P_2 = 1$), parallel ($P_2 = -0.5$), or isotropic ($P_2 = 0$). Thus, $P_1$ elucidates whether $P_2 = 1$ means that molecules are pointed up or down, and $P_2$ determines whether $P_1 = 0$ means that the film is isotropic or parallel.

**Figure 3** shows the substrate temperature dependence of the average molecular orientation within the prescribed bulk region. Consistent with experimental measurements and results from coarse-grained simulations of vapor-deposited films, that dependence found to be nonmonotonic. When $T_s$ is slightly below $T_g$, in this case 120 K $< T_s < T_g = 146$ K, there is a slight tendency for the molecules to orient perpendicular to the substrate ($P_2 > 0$) such that the ethyl groups are pointed toward the surface ($P_1 > 0$). For $T_s < 125$ K, the molecules start to orient more parallel to the substrate, with $P_2 < 0$ and $P_1$ decreasing toward zero after 125 K.

**Figure 4** provides the full $\cos(\alpha)$ distribution for the liquid-cooled glass and a subset of the PVD glasses (a larger subset is provided in SI Figure 7). For reference, a dotted line is shown to illustrate the uniform distribution that is expected for a completely isotropic film. The liquid-cooled glass exhibits a relatively uniform distribution, within some sampling error, as expected. For all PVD glasses the ethyl groups point away from the substrate to some degree. For the films just below $T_g$ there is a tendency toward slightly positive values, with a peak around $\cos(\alpha) = 0.75$ and monotonic decrease for lower cosine values as is evident for $T_s = 125$ K. For the films deposited at the lowest substrate temperature, 95 K, the peak is almost symmetric at $\cos(\alpha) = 0$. This is indicative of the molecules being oriented in the plane of the substrate, with very little perpendicular orientation. The substrate temperature $T_s = 115$ K represents the transition from the positively skewed distribution to the distribution of the lower $T_s$, with the peak located at zero with a relative plateau from 0 to 1.0.

In a previous coarse-grained study, Lyubimov et al. connected this $T_s$ dependent molecular orientation to features observed at the liquid–vacuum interface. We performed a similar analysis with ethylbenzene, but we focused on the rotational correlation during the deposition process with respect to the molecular orientation in the immobile state. In other words, where in the previous study the correlation was based on $P_2$ here we define for each molecule $i$ a quantity

$$p_i(t) = n_i(t) \cdot n_i^f = \cos(\delta_i)$$
where $n_i(t)$ is the molecular orientation unit vector of molecule $i$ at time $t$, $n'_i$ is the orientation of the final immobilized state, and $\delta_i$ is the angular displacement between them. The average rotational correlation with respect to $n'_i$ was calculated over the bulk molecules by

$$p_i(t) = \frac{1}{N_b} \sum_{i=1}^{N_b} p_i(t + t)$$

(6)

where $t_f$ denotes the moment in time when molecule $i$ was deposited on the free surface. The averaging was done over all molecules in the middle bulk region at the end of deposition, $N_b$. Similarly, the average depth into the film at time $t$ since deposition was defined by

$$\langle z_{\text{surf}}(t) \rangle = \frac{1}{N_b} \sum_{i=1}^{N_b} z_{\text{interface}}(t_i + t) - z_i(t_i + t)$$

(7)

where $z_{\text{interface}}(t_i + t)$ is defined by where the density drops to 50% of the bulk value in the $z$ dimension and $z_i(t_i + t)$ is the $z$ location of molecule $i$.

By plotting $p_i(t)$ with respect to $\langle z_{\text{surf}}(t) \rangle$ in Figure 5a, we get the average rotational correlation to the final immobilized orientation relative to film depth. All PVD films, except for those deposited at the two coldest $T_p$ start with zero or near-zero correlation to the final orientation. In accordance with what was observed for coarse-grained molecules, as the molecules become more deeply embedded into the film, the rotational correlation to the glass state $p_i(t)$ smoothly approaches unity. The curve shifts to the left as $T_p$ is lowered, indicating that the molecular orientation becomes frozen-in at shallower depths, and thus each molecule has a shorter period of time from when it is first introduced to when it is locked into the immobilized glassy state. For instance the films with $T_p = 95$ or 105 K are shifted such that the initial correlation value is as high as 0.25 at $\langle z_{\text{surf}}(t) \rangle \approx 0$. The immobilized orientation of the molecules deposited onto these films is correlated to the orientation of the molecules when they enter into first contact with the film.

Keeping with the procedure outlined by Lyubimov et al., we define a rotational arrest time, $t_{ar}$ through the relation $1 - p_i(t_f) = 1/e$ (horizontal dashed line of Figure 5a). The distance from the free surface at which this occurs is denoted by $z_* = \langle z_{\text{surf}}(t_{ar}) \rangle$. For each of the PVD glasses, the corresponding $z_*$ is marked by a vertical dashed line in Figure 5a (colored according to $T_p$). This gives a distance into the film at which the molecules become arrested, and thus a measure of how thick the mobile layer is during the vapor deposition process. There is a sudden shift between $T_p = 130$ K and $T_p = 140$ K due to the exponential temperature dependence of glass relaxation (SI). Figure 6.

Focusing on the equilibrium liquid films of ethylbenzene, there is a notable orientation preference at the vacuum–liquid interface, as was observed for the coarse-grained model and atomistic TPD simulations. Figure 5 panels b, c, and d show, respectively, the $P_1$ and $P_2$ order parameters and the density, $\rho_{\text{surf}}$, relative to the distance from the free interface, $z_{\text{surf}}$, for films held at four different temperatures above the effective $T_p$. As observed in previous studies, the density is relatively featureless, with a uniform profile prior to a monotonic decay at the interface, whereas $P_1$ and $P_2$ reach a maximum at a depth of about 0.4 nm, or half a molecular length. Right at the free surface, $P_1$ is near zero and $P_2$ is negative, indicating that the molecules are preferentially aligned parallel to the surface at first contact. For $z_{\text{surf}} \geq 0.8$ nm, or slightly larger than one molecular length, $P_1 = P_2 = 0$, indicating that molecular orientations are random for the bulk of the film. Between the free surface and 0.4 nm, $P_2$ goes from negative to slightly positive and $P_1$ becomes increasingly significant, Figure 5b,c. In this region, the molecules go from a preferential parallel orientation to one that is slightly oriented with the ethyl groups pointing toward the vacuum region. Deeper into the film, where 0.4 nm < $z_{\text{surf}}$ < 0.8 nm, both $P_1$ and $P_2$ decrease toward zero, indicating that the preferential order decays and the material becomes isotropic at these depths. The deviation from isotropic for $P_1$ and $P_2$ as $z_{\text{surf}} \to 0$ begins at the same point for each temperature, and the peak $z_{\text{surf}}$ for both order parameters remains the same. Moreover, $P_2$ switches sign and thus becomes parallel to the substrate at the same depth, for all considered temperatures refer to Figure 5c. However, as observed for the coarse-grained model, the height of the peak in the order parameters increases as the temperature approaches $T_p$.

Following the mechanism proposed in ref 28, we connect the $z_*$ to the values of $P_1$ at the same depth into the film (dashed lines from panel a to panel b in Figure 5). In Figure 6, we compare the values of $P_1$ for each $T_p$ (black) with the values for $T = 170$ K corresponding to $z_*$ defined by either $1 - p_i(t_f) = 1/e$ (red) or $1 - p_i(t_f) = 0.5$ (blue). All curves have relatively the same shape, though the predicted values for $1/e$ are shifted to the left and peak at 125 K whereas the measured values peak at 120 K. Defining $z_*$ based on $1 - p_i(t_f) = 1/e$ is rather arbitrary, though inspired by typical exponential decay. This value of $1/e$ could be shifted in order to more properly fit the measured
data, but the relative correlation between the orientation at the free surface of the film and the liquid and what is observed in the PVD glasses would remain. For instance, \( z_a \) based on \( 1 - p_1(t_a) = 0.5 \) provides a similar peak position, thus the corresponding curve is in better agreement with the observed \( P_1 \) values (Figure 6 blue). We also note that the analysis outlined above and shown in Figure 6 is more clearly manifest on \( P_1 \) than it is on \( P_2 \).

The previous characterizations neglected to address a component of structural ordering crucial to charge transport: the orientational correlations between neighboring molecules. The relative orientation of the pi-systems for two ethylbenzene molecules, described by the normal vector of each benzene ring, will, when taken in conjunction with their separation distance, be directly related to the magnitude of the electronic transfer integral.\(^{36} \) To examine these local correlations, we plotted the alignment probability as a function of neighbor distance (SI Figure 8). While from SI Figure 8 it is apparent that there is a slight enhancement in the ordering of local molecular orientations for the 120 K PVD film relative to the liquid-cooled film, the change is very subtle. Whereas in more practical molecular semiconducting molecules we expect a stronger correlation due to pi-stacking effects, for benzene, it is well-known that the pi-stacking configuration is not a global minimum energy configuration relative to the “T-structure”, and many competing minimum energy configurations exist.\(^{37} \) Consequently, there is no expectation of pi-stacking being the deeper energy minimum configuration within the stable glasses.

To further explore the nature of the orientational correlation networks within the films, we have used a graph-theoretical approach inspired by previous work\(^{38} \) and constructed adjacency matrices using correlation functions between neighboring ethylbenzene molecules. By examining the eigenvalues of the corresponding Laplacian matrix, we use the algebraic connectivity as a measure of structural correlations within these graphs.\(^{39} \) As observed in the Supporting Information, the enhancement of the graph’s connectivity for the 120 K PVD film is slightly increased relative to the liquid-cooled film, but the effect is within the error bars of both

![Figure 6. Value of \( P_1 \) from the 170 K equilibrium liquid at the \( z_{surf} \) where \( p_1(t) = 1 - 1/e = 0.632 \) (red) and 0.5 (blue) for the given substrate temperature from Figure 5a,b.](image)

Figure 7a shows the distribution of site energies corresponding to the valence hole band of ethylbenzene for the vapor-deposited glass at 120 K normalized to the mean site-energy value, and a similar plot is provided in SI Figure 9a for the liquid-cooled glass (\( q_c = 1 \) K/ns). The distributions fit well to a Gaussian distribution of site energies, as is commonly considered in organic semiconducting materials.\(^{40} \) Fitting the standard deviation of the site energies yields a site-energy disorder parameter of 222 ± 2.6 meV for the liquid cooled glass, and 201 ± 1.3 meV for the vapor-deposited glass, using a simple bootstrapping analysis for the error. While this difference appears small, it is quite consequential, particularly given the fact that the stability and orientational effects in simulated systems are significantly less than experimentally observed, that ethylbenzene is a relatively nonpolar molecule, and that actual organic semiconducting molecules of relevance will be significantly larger, thus exhibiting greater potential for orientational preferences. As such, this \( \approx 20 \) meV difference in energetic disorder is considerable. Typical values of the site-energy disorder range between 0 and 300 meV, making this 10% change for ethylbenzene an important consideration for molecular design, especially provided that larger, more anisotropic molecular semiconductors used in practical applications should exhibit

![Figure 7. Histograms of (a) the molecular site energies in eV and (b) the transfer integrals (eV) for the 120 K vapor-deposited glass.](image)
larger orientational preferences than our minimal ethylbenzene model.31

Figure 7b shows the distribution of transfer integrals for the vapor-deposited glass at 120 K (see the Supporting Information for distribution of liquid-cooled glass). Computing the mean-squared electronic coupling for this system, which is the relevant prefactor in a nonadiabatic rate expression, yields 23.08 ± 0.01 meV for the vapor-deposited glass and 21.04 ± 0.02 meV for the liquid cooled glass. This 2 meV increase in the RMS transfer integral is substantial, as the maximum value of the transfer integrals in these systems in which Marcus-like theories apply is 25 meV. Consequently, we again observe an approximately 10% effect in the enhancement of the electronic couplings between stable ethylbenzene glasses and conventional liquid-cooled glasses.

The enhancement in the transfer integral and the decrease of structural disorder can be directly related to the structural ordering of the system.41 In the case of the transfer integral, its enhancement could conceivably arise from two effects. First, all neighboring ethylbenzene molecules are on average closer together for the 120 K PVD glass due to the relatively higher density, and thus the transfer integrals (which depend exponentially on the relative separation of the COG) will increase. Second, the increase in the neighboring orientational correlations between ethylbenzene molecules was shown to marginally increase (see the Supporting Information), and the overlap of the pi-orbital systems should consequently increase.36 We have evidence for both effects contributing here, though it is our expectation that the relative importance of the density-dependent effect and the orientational-dependent effect do not properly represent common organic semiconductors, as the pi-stacking configuration of two ethylenzene molecules is not a deep global minimum,37 as it is in the majority of practical molecular semiconductors with significantly larger pi-electron systems.32

Regarding the decrease in the site-energy disorder, this effect is in agreement with the observed trends in the structural ordering of the films. Since the site energy of the hole state of a molecule depends strongly on the relative orientation of the neighboring dipoles,35 the increased structural ordering of the film should lead, on average, to a more uniform dipolar environment around each ethylbenzene molecule,31 leading to decreased energetic disorder.

A third effect which influences charge transport in these systems, and which could potentially be tuned by PVD, is the role of the charge transport network topology.38 For a hopping charge to traverse the length scale of a device, it must depend not upon single molecule properties alone, but on the correlated hops between a number of aligned molecules (a one-dimensional stack of pi-electron entities). Given the inherent weakness of van der Waals forces relative to thermal energy, the self-assembly of these molecules over device length scales is difficult. PVD presents a potentially useful mechanism for the alignment of charge transport entities over length scales larger than that dictated by van der Waals forces alone. Previous experimental work has described the importance of molecular orientation effects for charge transport and light-emitting diode applications, where the specific alignment of molecules over large length scales can lead to considerable optoelectronic enhancements.38 While our graph-theoretical orientational correlation function is a step in this direction, the full analysis of the topology of the charge transport network, and how this varies with deposition conditions, could be integral to inducing directional charge transport within the deposited films. Work is currently underway studying this effect in more practical organic semiconductors, where the local orientational ordering and, thus, the charge transport topology depend on a deep pi-stacking minimum, and are more strongly modified by the PVD process.

**CONCLUSIONS**

These simulations make a series of predictions about the structure of vapor-deposited glasses of ethylbenzene in line with known experimental observables, as indicated by the computed glass transition temperature and fragility. Vapor deposition onto substrates with temperatures ranging from 95 to 145 K led to films with enhanced kinetic stability and lower inherent structure energies relative to liquid-cooled glasses; the onset temperatures were found to be up to 11 K above those of liquid cooled films. The substrate–temperature dependent anisotropic behavior observed in past studies of larger molecules was demonstrated to also occur for this smaller molecule. These calculations indicate that even slightly anisotropic molecules can result in anisotropic glasses when vapor deposited. Consistent with past work for coarse-grained TPD molecules by Lyubimov et al.,36 the anisotropic molecular orientation in the films can be traced back to molecular ordering observed at the vacuum interface of the equilibrium liquid.

Using ethylbenzene as a minimal model for common organic semiconducting molecules, we also examined the effects of PVD-induced structural effects on molecular descriptors relevant to charge transport, specifically the distribution of site energies and the transfer integrals between molecular sites. Our simulations demonstrate a 10% (≈20 meV) decrease in energetic disorder and a 10% (2 meV) enhancement of the mean-squared transfer integrals within the vapor-deposited film, relative to the slowest liquid cooled film. Given the under-prediction of structural order in simulated films relative to experimental films, and the larger, more anisotropic dimensions of organic semiconductors used in practical semiconducting devices, we expect these effects to be potentially considerable in stable glasses of common organic semiconductors. Moreover, the ability of PVD to tailor the global molecular orientation of molecules in a stable glass film has potential ramifications for tailoring the topology of charge transport networks, an idea which will be explored in future work.

**METHODS**

**Simulated Vapor Deposition.** Atomistic simulations of ethylbenzene (EB) films were performed with the all-atom optimized potential for liquid simulations (AA-OPLS) force field.34,45 The substrate was constructed of Lennard-Jones particles with characteristic energy and size similar to those of silica (σ = 3 Å, ε = 5.2 kJ/mol, mass = 60, and density = 2650 g/L) as used in previous all-atom PVD simulations.40 Each substrate atom was restrained to its initial position through a harmonic potential, where the spring constant was K = 10^7 kJ/ (mol nm^2). The volume of the system was held constant with box dimensions 5 nm × 5 nm × 20 nm, and periodic boundary conditions were enforced in the lateral directions. The x and y dimensions are about 7 times the molecular length of EB (≈7.25 Å). The length of the box in the z direction (perpendicular to the substrate) was sufficiently large to encompass the film during deposition, with ample amount of vacuum space to avoid interaction between the top layer of the
molecule in this region, a 2-level ONIOM\(^\text{55}\) (B3LYP/6-31G* in the glass was examined for charge transport. For every molecule, the heating and cooling runs, temperature coupling was constrained using the SETTLE\(^\text{51}\) and LINCS\(^\text{52}\) algorithms. All simulations were performed with a time step of 2 fs. A stochastic integrator was used during the vapor deposition process described below.\(^\text{53}\) This choice was made due to the small number of atoms being coupled to the thermostat at certain points of the process. During production runs, including the heating and cooling runs, temperature coupling was achieved using velocity rescaling with a stochastic term.\(^\text{44}\)

The deposition cycle consists of six repeated steps: (i) introduction of two randomly oriented molecules within 1.5 molecular lengths above the film surface (red in SI Figure 11b), (ii) minimization of the energy for the entire system using the conjugate gradient method, (iii) equilibration of the newly introduced molecules at high temperature (\(T = 200\) K) for 200 ps, (iv) linear cooling over a period of 1200 ps of the newly introduced molecules to the substrate temperature, (v) a short equilibration of these molecules at the substrate temperature for an additional 200 ps, and finally (vi) minimization of the energy for the entire system. A separate thermostat is used to maintain the previously deposited molecules and substrate particles at the desired substrate temperature throughout the cycle. Any molecules that remain in the vacuum region, dissociated from the film at the end of a deposition cycle, are deleted to avoid the formation of separate aggregates. The energy is minimized at the start and end of the cycle, as discussed in previous work,\(^\text{46}\) in order to help relax the films during the relatively shorter time scales that are accessible to simulations compared to those used in experiments. This process was repeated until all the films have at least 1200 or more EB molecules inserted, which in the glass state corresponds to a film thickness of about 8 nm (SI Figure 10).

The bulk of the film was defined to be from 4.8 to 7.2 nm in the \(z\) dimension, or roughly 3.3 molecular lengths thick. These limits are based on where the substrate effect in the density fluctuations is dampened and where the Debye–Waller factor becomes relatively constant before rapidly increasing again near the free interface, as demonstrated for the three samples deposited at \(T_s = 130\) K (0.89\(T_\text{g}\)) in SI Figure 10 and highlighted in SI Figure 11b. The Debye–Waller factor, denoted by \(\langle u^2 \rangle\), is defined as the average mean-squared displacement of hydrogen atoms after 20 ps; this is a commonly measured quantity that can be extracted both from neutron scattering experiments and from simulations, and it provides a measure of local mobility and free volume. Three independent films were deposited for each substrate temperature, and five independent samples were used to generate statistically meaningful results for the liquid-cooled films.

**Energetic Disorder for Charge Transport.** The bulk region of the glass was examined for charge transport. For every molecule in this region, a 2-level ONIOM\(^\text{55}\) (B3LYP/6-31G*:CHARMM) optimization was performed on the cationic state for the ethylbenzene molecule within a frozen shell of nearest neighbors (cutoff = 7 Å). The cation state represents the electronic state of interest for hole transport in a molecular semiconducting film. Our ONIOM methods treat the center molecule at the DFT level (B3LYP/6-31G*), and the nearest neighbor shell with molecular mechanics (CHARMM). This modest basis set size is necessary for the calculation of energetic disorder over the entire film width to be performed in a reasonable amount of computer time. The ONIOM optimization yields a local site energy for every molecule in the film, which is dictated by the precise arrangement or packing of the neighboring molecules. Site energies are computed for all molecules in the region and histogrammed over the film width, with subsequent averaging for five trajectory snapshots for three separate trajectories for both the conventional liquid-cooled glass and the 120 K vapor-deposited glass. The histogram is then plotted and fitted to a Gaussian disorder model to obtain the standard deviation of the site energies.\(^\text{40}\) Note that a larger standard deviation of the site energy implies more energetic disorder, and has a deleterious effect on charge transport. All electronic structure calculations involved in the determination of site energies were performed using the Gaussian software package.\(^\text{46}\)

**Transfer Integrals for Charge Transport.** Each molecule surrounded by “\(N\)” nearest-neighbors within the 7 Å cutoff was parsed into \(N\) separate snapshots where the transfer integral for hole self-exchange between two ethylbenzene sites is determined using the Electron Transfer module\(^\text{57}\) in NWChem at the B3LYP/6-31G* level of theory. The self-exchange reaction can be denoted \((\text{EB}/\text{EB}^+) \rightarrow \text{EB}^+ + \text{EB}\), where \(\text{EB}^+ + \text{EB}\) and \(\text{EB}^+\) represent the cation state and ground state of ethylbenzene, respectively. Transfer integrals between all nearest neighbors are computed for all molecules in the film, with subsequent averaging for five trajectory snapshots for three separate trajectories for the liquid-cooled and vapor-deposited morphologies. The mean-squared electronic coupling is then determined from the distribution of transfer integrals in the film. This mean-squared coupling would be the exact input used in a Marcus-like approach to charge transfer theory,\(^\text{53}\) and thus the larger its value, the more beneficial for charge transport within the film.
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