

Article

# Probing Glass Formation in Perylene Derivatives via Atomic-Scale Simulations and Bayesian Regression

Eric Lindgren, Jan Swenson, Christian Müller, and Paul Erhart\*

Cite This: J. Phys. Chem. B 2025, 129, 6613–6619 ACCESS Metrics & More Article Recommendations Supporting Information ABSTRACT: While the structural dynamics of chromophores are of interest for a range of applications, it is experimentally very challenging for resolve the underlying microscopic mechanisms. At the same time,

interest for a range of applications, it is experimentally very challenging to resolve the underlying microscopic mechanisms. At the same time, glassy dynamics are also challenging for atomistic simulations due to the underlying dramatic slowdown over many orders of magnitude. Here, we address this issue by combining atomic scale simulations with autocorrelation function analysis and Bayesian regression, and apply this approach to a set of perylene derivatives as prototypical chromophores. The predicted glass transition temperatures and kinetic fragilities are in semiquantitative agreement with experimental data. We suggest that the remaining error could be caused by an overestimation of the intermolecular cohesion by the force field used



in this work. By analyzing the underlying dynamics via the normal vector autocorrelation function, we are able to connect the  $\beta$  and  $\alpha$ -relaxation processes in these materials to caged (or librational) dynamics and cooperative rotations of the molecules, respectively. The workflow presented in this work serves as a stepping stone toward understanding glassy dynamics in many-component mixtures of perylene derivatives and is readily extendable to other systems of chromophores.

#### INTRODUCTION

Chromophores are an important class of materials with a range of potential and realized applications in the area of energy conversion thanks to their exceptional optical properties. Chromophores have been studied, e.g., as active materials in solar cells,<sup>1-5</sup> organic light-emitting diodes,<sup>6,7</sup> and photoswitchable and solar thermal storage systems.<sup>8-1</sup> The properties of these materials are sensitive to both the structural arrangements of the molecules and their dynamic behavior. The dynamics as manifested in macroscopic properties such as viscosity and diffusivity, are also important for solution processing, which is currently the most common approach for large-scale manufacturing of devices based on these materials. Controlling viscosity and diffusivity is often achieved through glass formation,<sup>11</sup> which can occur upon rapid cooling, bypassing crystallization and resulting in a glassy state that lacks long-range order. The glass transition is characterized by a dramatic slow down in the materials dynamics over a narrow temperature range that is commonly probed via the temperature dependence of, e.g., the viscosity (via rheometry), the density (via dilatometry) or the heat exchanged with the environment (via calorimetry).

For practical use, it is crucial to achieve glass formation controllably at modest cooling rates. In this context, using mixtures of perylene derivatives, it has been shown that increasingly stronger glass formers can be systematically obtained by increasing the number of components. This principle works even though the underlying molecules are weak ("fragile") glass formers in single-component systems.<sup>12</sup> Moreover, it has been found that such many-component mixtures have further benefits, including significantly improved thermal stability.<sup>13</sup> While many-components mixtures thus have very high potential for materials design, the much larger design space also renders understanding the underlying dynamical processes much more challenging. Here, as a first step toward a systematic understanding of these materials, we investigate glass formation in single-component liquids of perylene derivatives (Figure 1a) using molecular dynamics (MD) simulations in combination with Bayesian regression.

While the microscopic dynamics of glass-forming systems can be explored via MD simulations,<sup>14,15</sup> it is usually challenging to directly access the temperature range in which the glass transition occurs due the time-scale limitations of this technique, although there are cases in which it is possible.<sup>16</sup> Here, to extend the temperature range, we combine MD simulations with Bayesian regression, which allows us to predict glass transition temperatures as well as the propensity for glass formation (expressed via the kinetic fragility). To this

 Received:
 February 6, 2025

 Revised:
 June 1, 2025

 Accepted:
 June 2, 2025

 Published:
 June 23, 2025







**Figure 1.** (a) Perylene derivatives studied in this work. (b) Schematic representation of the normal vector autocorrelation function  $J(\tau)$ , see eq 2.

end, we observe the temperature dependence of the dynamics via the diffusivity, which is anticorrelated with the viscosity but computationally easier to converge than the latter. Our results for the glass transition temperatures and the kinetic fragility are in semiquantitative agreement with experimental data, supporting the viability of the simulation approach. To gain insight into the microscopic processes we analyze the time-autocorrelation function (ACF) of the molecular orientation, which reveals three distinct dynamic regimes corresponding to intramolecular motion as well as  $\beta$  and  $\alpha$ -relaxation processes. Our work thereby establishes the viability of this simulation approach and lays the groundwork for future studies of the evolution of the dynamics in many-component mixtures.

#### METHODS

We considered five perylene derivatives (Figure 1a), which differ with respect to the length *n* of the pendant alkyl chain  $C_nH_{2n+1}$  attached to one of the bay positions. Monomer I corresponds to regular perylene with no alkyl chain, whereas monomers II–V have alkyl chains containing two (n = 2), four (n = 4), six (n = 6), and 12 (n = 12) carbon atoms, respectively.

Diffusivity and Autocorrelation Functions. To characterize the dynamics of the perylene derivatives, we first consider the molecular diffusivity *D*, which can be obtained from the MSD  $\langle \Delta r^2 \rangle$  of the molecular centroid positions<sup>17</sup>

$$\left\langle \Delta r^2 \right\rangle = 6D\tau \tag{1}$$

The diffusivity was computed using production runs with a duration of up to 10 ns.

To obtain more detailed insight into the underlying microscopic properties, we also analyzed the ACF of the normal vectors indicating the orientation of each individual molecule (Figure 1b) given by

$$J(\tau) = \left\langle \hat{\boldsymbol{n}}_{i}(t) \cdot \hat{\boldsymbol{n}}_{i}(t+\tau) \right\rangle_{it}$$
<sup>(2)</sup>

Here,  $\hat{n}_i(t)$  is the normal vector of molecule *i* (Section S1). The ensemble average applies over all times *t* and each molecule *i* in the system. Equation 2 can be efficiently evaluated using the Wiener-Kinchin theorem.

One may also extract the standard error as an uncertainty estimate for  $J(\tau)$  from the ACF for each molecule  $J_i(\tau)$  before computing the ensemble average in eq 2 according to

$$\sigma_{J}(\tau) = \sqrt{\operatorname{Var}(\{J_{i}\}_{i=1}^{N})/N}$$
(3)

where N is the number of molecules in the system.

Since the ACFs spans multiple orders of magnitude in time, production runs of different length were conducted. To sample short and long-time scales, simulations with a length of respectively 100 ps and 10 ns were carried out with snapshots being written every 1 and 100 fs, respectively (Section S1). The normal vector ACFs were calculated for both production runs and subsequently spliced together at a time lag of 1 ps.

**Computational Details.** MD simulations were performed using the GROMACS package<sup>18</sup> (version 2021.3) with the OPLS all-atom force field.<sup>19</sup> Topology and structure files where generated using the LigParGen server,<sup>20–22</sup> starting from structures from the automated topology builder and repository.<sup>23–25</sup> The per-atom charges obtained from the



**Figure 2.** (a) Extrapolation of the temperature dependence of the Vogel–Fulcher–Tammann (VFT) fit of the diffusivity to lower temperatures (see Section S2 in the Supporting Information for the MD data). The glass transition temperature  $T_g$  is defined as the temperature where the mean squared displacement (MSD) over 100 s reaches 100 Å, denoted by the horizontal gray dashed line. The error band corresponds to one standard deviation. (b, c) Violin plots of (b) the glass transition temperature  $T_g$  and (c) the kinetic fragility *m* estimated from both the diffusivity and the normal vector ACF. Experimental values are from ref 12.  $T_g$  values were experimentally obtained from differential scanning calorimetry (DSC) first heating thermograms with a heating rate of 0.17 K·s<sup>-1</sup>. The kinetic fragility was obtained from fast scanning calorimetry (FSC) measurements for various cooling rates as  $m = -d \log|q|/d(T_g/T_f')|_{T_t'=T_s'}$  where *q* is the cooling rate and  $T_f'$  is the fictive FSC temperature. The simulated values for the kinetic fragility were computed from the VFT parameters as  $m = BT_g/[\ln(10) \cdot (T_g - T_{VF})^2)]$ . Note that  $T_g$  is typically not observed experimentally for derivative I, due to its strong tendency to crystallize.

LigParGen server where slightly modified in order to obtain neutral molecules. A time step of 1 fs was used for all simulations, in combination with constraining the hydrogen atoms using the linear constraint solver algorithm.<sup>26</sup> The simulation cell contained between 500 and 2000 molecules depending on the length of the alkyl chain of the perylene derivative, and simulations were performed at temperatures in the range 400–800 K.

Each system was equilibrated at the target temperature prior to production using the following protocol. First, the system energy was minimized using a steepest descent optimizer, after which a simulation of 1 ns was performed in the *NVT* ensemble. This was followed by a 1 ns run in the *NPT* ensemble at a pressure of 2 kbar using a Berendsen barostat<sup>27</sup> to avoid cavitation. The high-pressure *NPT* simulation was followed by a 10 ns *NPT* simulation at 1 bar. Finally, production runs were carried out in the *NPT* ensemble using the stochastic pressure-rescaling barostat and a stochastic velocity-rescaling thermostat<sup>28</sup> to obtain the diffusivity as well as the short and long-time normal vector ACF (Section S1). The production runs were 100 ps and 10 ns long, and trajectory files were written every 1 and 100 fs, respectively.

The trajectories resulting from the simulations were then parsed using the MDTRAJ package<sup>29</sup> and analyzed using PYTHON scripts to compute the correlation function defined by eq 2. Bayesian regression analysis was performed using the NUMPY,<sup>30</sup> PANDAS,<sup>31,32</sup> SCIPY<sup>33</sup> and EMCEE<sup>34</sup> packages. Plots were generated using MATPLOTLIE,<sup>35</sup> SEABORN,<sup>36</sup> CORNER,<sup>37</sup> and color maps from PERFECT-CMAPS.<sup>38</sup> Finally, structures were visualized and rendered for publication using OVITO.<sup>39</sup>

#### RESULTS

Glass Transition and Kinetic Fragility. We begin by analyzing the temperature dependence of the molecular diffusivity (Figure 2a; also see Section S2). When obtaining these data from MD simulations we are limited by the time scale that is reachable via the latter. While one can reach on the order of 1  $\mu$ s in total simulation length, the diffusivity rapidly decreases as the temperature is lowered. At lower temperatures, diffusion events become so infrequent that molecules appear immobilized on the MD time scale. Assuming a nearest neighbor distance of 3 Å and a simulation length of 10 ns, this implies that the diffusivity can no longer be reliably estimated if its value drops below approximately 9 Å<sup>2</sup>/10 ns  $\approx 10^{-14}$  m<sup>2</sup> s<sup>-1</sup>. For the present system, this is the case for temperatures below approximately 400 K (see Section S2 of the Supporting Information for an extended analysis). This is below the experimental melting point of pure perylene of around 550 K but above the experimental glass transition temperatures, which range around 250 K.<sup>12</sup>

In order to be able to gain information about the behavior at these temperatures, we need to extrapolate. However, since the diffusivity and other properties change rapidly over many orders of magnitude in this region, this extrapolation must be done with care and account for error propagation. To this end, we employ the VFT equation and combine it with Bayesian regression. The former describes the temperature dependence of, e.g., the viscosity or the diffusivity of fragile glass formers, allowing for non-Arrhenius behavior. While the VFT equation is empirical in nature, it is widely used in the analysis of glassforming systems and provides an accurate fit for many experimental observations as well as the data obtained here (Figure 2a). For the diffusivity it reads ,

$$D(T) = D_0 \exp[-B/(T - T_{\rm VF})]$$
(4)

where  $D_0$  is a prefactor,  $T_{\rm VF}$  is the Vogel–Fulcher temperature, and *B* is a parameter akin to a pseudoactivation energy.<sup>40</sup> The parameters of the VFT equation can in turn be used to compute the kinetic fragility  $m = BT_g/[\ln(10) \times (T_g - T_{\rm VF})^2)]$ , where  $T_g$  is the estimated glass transition temperature.<sup>41,42</sup>

Due to the exponential in eq 4 extrapolation and error propagation require care, which we handle here via Bayesian regression. The latter is a technique in which a model  $M(\theta)$ with parameters represented by a parameter vector  $\theta = [D_0, T_{\text{VF}}, B]$  is fitted to a set of data  $\mathcal{D}$  given prior information I, using Bayes' theorem

$$p(\boldsymbol{\theta}|\mathcal{D}, I) \propto p(\mathcal{D}|\boldsymbol{\theta}, I)p(\boldsymbol{\theta}|I)$$
(5)

The advantage of a Bayesian approach is 2-fold. First, prior beliefs are clearly stated in the prior distribution  $p(\theta|I)$ . Second, error estimates are readily extractable from the posterior distribution  $p(\theta|D, I)$ , since data uncertainties and errors can be encoded in the likelihood function  $p(D|\theta, I)$ . We then sample the posterior distribution  $p(\theta|D, I)$  via Markov-chain Monte Carlo (MCMC) simulations using the diffusivity data from MD simulations to fit the VFT equation (see Section S3 for details). This allows us to extrapolate the diffusivity to lower temperatures along with controlled error estimates (Figure 2a).

The temperature at which the system transitions into a glassy state is denoted by the glass transition temperature  $T_g$ .  $T_g$  cannot be uniquely defined but is rather set by a pragmatic property-dependent threshold. For example, one often takes  $T_g$  as the temperature where the viscosity reaches a value of  $10^{11}$  Pa·s.<sup>42</sup> In the present work, when considering the diffusivity, we adopt a threshold of  $17 \times 10^{-22}$  m<sup>2</sup>/s, which corresponds to a MSD of 100 Å<sup>2</sup> over 100 s. In other words, it specifies the onset of diffusion beyond the first-nearest neighbor shell. We emphasize that since the viscosity and similarly the diffusivity change very steeply around the glass transition (Figure 2a) the threshold value has only a modest effect on the values obtained for  $T_g$ . For example, increasing or decreasing the threshold by 2 orders of magnitude changes our estimates for  $T_g$  by only ±5 K.

The glass transition temperatures obtained here are in semiquantitative agreement with experiments, and correctly predict the trend from II to  $V^{12}$  (Figure 2b). However, the simulated  $T_g$  values are overestimated compared to experimental values obtained by differential scanning calorimetry (DSC) by 50–70 K. The predicted kinetic fragilities are also in agreement with experimentally obtained values from fast scanning calorimetry (FSC) (Figure 2c).

The glass transition temperature decreases systematically with increasing alkyl chain length. Conceptually, this can be explained by an increase in the effective volume available to each molecule caged by its neighbors, due to the longer pendant groups. It is, however, noteworthy that the kinetic fragility exhibits a maximum for III, which features a butyl pendant chain—a nontrivial behavior that is observed in both experiment and simulation.

**Revealing the Relaxation Processes.** We now turn to the normal vector ACF  $J(\tau)$  (eq 2) to gain further insight into the relaxation processes close to the glass transition (Figure 3a). We demonstrate the procedure for obtaining the



**Figure 3.** Bayesian regression workflow used to extrapolate the normal vector ACF to longer time scales. (a) Normal vector ACFs for perylene derivative I at different temperatures. Note that the *y*-axis has been split using different scales to reveal the multiple steps in the ACF. (b) Normal vector ACF for perylene derivative I at 45 K along with the corresponding posterior distribution of fits to eq 6. (c) Subset of the posterior distribution in (b),  $p(\tau_1, \tau_2, \tau_3 | D, I)$ , shown as a corner plot. (d) Fit to the VFT expression eq 7 using the mean  $\mu$ , and standard deviation  $\sigma$  of the marginal distribution  $p(\tau_3 | D, I)$ .

temperature dependence of  $J(\tau)$  for derivative I, noting that the general temperature dependence of  $J(\tau)$  is consistent for all perylene derivatives I–V (see Supporting Information Section S4 for the ACFs for all perylene derivatives).

First, we observe that the correlation time of  $J(\tau)$  depends strongly on temperature, ranging from 100 ps at 800 K to >10 ns at 400 K. At 800 K the perylene molecules thus maintain their orientation over a time scale on the order of 100 ps, while they are effectively locked in their orientation over 10 ns at 400 K.

Second, the ACFs can be described by the sum of two exponential functions and one stretched exponential function, where the latter is a common feature of correlation functions in glassy systems<sup>43</sup>

$$J(\tau) = A_1 e^{-\tau/\tau_1} + A_2 e^{-\tau/\tau_2} + (1 - A_1 - A_2) e^{(-\tau/\tau_3)^{\beta}}$$
(6)

The time scales  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$  are separated by several orders of magnitude at low temperatures, with  $\tau_1 \approx 0.1$  ps,  $\tau_2 \approx 10$  ps, and  $\tau_3 \approx 1$  ns at 450 K.  $\beta \leq 1$  is the stretch exponent for the long time scale component.

We can apply the same Bayesian regression workflow as for the diffusivity to estimate the glass transition temperature and kinetic fragility from the temperature dependence of the normal vector ACF. However, an additional step is required compared to the diffusivity, as the normal vector ACF needs to be fitted to eq 6 for each temperature (Figure 3b). Each fit yields a full posterior probability distribution  $p(A_1, A_2, \tau_1, \tau_2, \tau_3, \beta | T, D, I)$ . An estimate for the time scale of the slowest process captured by the ACF presented by  $\tau_3$  with uncertainty estimates can then be obtained from the marginal distribution  $p(\tau_3 | T, D, I)$  for each temperature (Figure 3c). A VFT equation of the form

$$\tau_3(T) = \tau_0 \exp[B/(T - T_{\rm VF})]$$
(7)

is then fitted to the temperature dependence of  $\tau_3$ , which allows for a similar extrapolation to longer time scales as in the case of the diffusivity (Figure 4). Here, the threshold for  $\tau_3$ above which the system is deemed to be in a glassy state was again taken to be 100 s.<sup>42</sup> Note that the resulting glass transition temperature is relatively insensitive to this particular



**Figure 4.** Extrapolation of the temperature dependence of the slowest process represented by  $\tau_3(T)$ , to lower temperatures and thus lower frequencies. The error band corresponds to  $\pm$  one standard deviation.  $T_g$  is defined to be the temperature which the time scale reaches 100 s, represented by the horizontal gray dashed line.

threshold, as increasing or decreasing the threshold by 2 orders of magnitude only changes  $T_{\rm g}$  by  $\pm 7$  K.

The estimates for both the glass transition temperature and the kinetic fragility from the normal-vector ACF and the diffusivity generally agree with each other (Figure 2b,c). Both schemes capture the trend of decreasing T<sub>g</sub> with increasing length of the alkyl chain of the perylene derivative. However, the estimates from the diffusivity are higher than those from the normal-vector ACF typically by 10-30 K for the glass transition temperature and by 10-40 for the kinetic fragility. This difference is due to the two observables probing different processes. The diffusivity is sensitive to the diffusion of the monomers, while the normal vector ACF probes the rotational motion of the monomer. The normal vector ACF and the diffusivity are thus complementary. The difference in  $T_{g}$ between both observables suggests that the monomers continue to rotate on long time scales 10-30 K below the temperature at which diffusion has slowed down.

We can elucidate the relaxation processes in the system by decomposing the ACF into the contribution of each exponential function that make up  $J(\tau)$  (Figure 5). The separation of time scales between the processes allows the



**Figure 5.** Decomposition of the normal vector ACF  $J(\tau)$  into individual exponential functions representing three different relaxation processes. The fastest process with a correlation time of about 0.1 ps at 450 K corresponds to intramolecular atomic motion. The second one ( $\beta$ -relaxation) with a correlation time of approximately 10 ps at 450 K corresponds to librational motion and twisting of the perylene core. Finally, the slowest process ( $\tau_3$ -relaxation) with a correlation time of approximately 10 ns at 450 K corresponds to the hindered rotational reorientation of the perylene molecules due to intermolecular interactions.

selective application of frequency filters in the Fourier domain, corresponding to the time scales represented by  $\tau_1$ ,  $\tau_2$ , and  $\tau_3$ . These filters are applied to the trajectory of a single perylene molecule extracted from the entire MD trajectory, and allows us to single out the dynamics that correspond to each process (see the supplementary movie for a visual representation of this scheme, and Section S5 of the Supporting Information for further details).

We study the dynamics of perylene derivative I at a temperature of 450 K as an example of this scheme (Figure 5). The fastest process with time scale  $\tau_1$  corresponds to intramolecular atomic motion. The second fastest process,  $\tau_{2}$ , corresponds to  $\beta$ -relaxation enforced by caging by neighboring molecules, such as libration and twisting of the perylene core. Neither the  $\tau_1$  nor the  $\tau_2$  processes significantly affect the orientation of the molecule, as is evident by their small amplitude. The bulk of the autocorrelation function  $J(\tau)$  is made up of the slow  $\tau_3$  process.  $\tau_3$  corresponds to cooperative intermolecular processes, such as reorientation of molecules. The reorientation of a molecule requires neighboring molecules to rotate, which takes place over rapidly increasing time scales as the temperature is decreased. The experimental and simulated values of the kinetic fragility indicate that all derivatives studied in this work are fragile glass formers. In fragile glass formers, the level of cooperation decreases significantly at temperatures greater than  $T_{\rm g}^{44}$  That  $au_3$  captures cooperative reorientation even in the supercooled regime at

450 K thus indicates that it is sensitive to processes that are more prominent close to the glass transition in fragile glass formers. Based on this, we attribute  $\tau_3$  to be related to  $\alpha$ relaxation, and that the microscopic mechanism driving glass formation in perylene derivatives **I**-**V** is the cooperative reorientation of the molecules.

#### DISCUSSION

Given the sources of uncertainty related to the underlying empirical force field used in the MD simulations and the extrapolation over many orders of magnitude, we consider the overall agreement of the predicted glass transition temperatures and kinetic fragilities with the experimental data very encouraging. The normal vector ACF in particular show semiquantiative agreement with experiments, with the ACF systematically yielding both lower glass transition temperatures and kinetic fragilities than the diffusivity (Figure 2b,c). This difference highlights the complementarity of the diffusivity and the normal vector ACF, as they are more sensitive to molecular diffusion and rotation, respectively. The estimated higher value of the glass transition temperature from the diffusivity can be understood as molecular diffusion freezing in at a higher temperature compared to rotation. The processes driving glass formation are thus cooperative rotational processes, as elucidated by the decomposition of the normal vector ACF. This is supported by the large kinetic fragility deduced for all derivatives (Figure 5). Capturing both diffusion and rotation is hence key in order to accurately describe the relaxation processes in the fragile perylene derivatives studied in this work.

Both the normal vector ACF and the diffusivity systematically overestimate the glass transition temperature and the kinetic fragility compared to experiment. The overestimation of the kinetic fragility suggests that the processes represented by  $\tau_3$  in the MD simulation are slower than those encountered during experiments. This could be caused by the intermolecular interactions in the simulation being somewhat too soft, which would point toward a limitation in the accuracy of the underlying force field. Another possible explanation could be that the normal vector ACF overestimates the time scale of processes in the system. Third, the VFT equation is an empirical model, and extrapolating to lower temperatures may introduce a systematic error.<sup>45</sup> In order to go beyond empiricism, more explicit characterizations of the glass dynamics, e.g. mode coupling theory, could be pursued.<sup>46,47</sup>

As noted in the introduction, experimentally the glass transition can also be detected as a change in the thermal expansion of the material, an approach that is also occasionally adopted in simulations. $^{16,48-53}$  It is therefore instructive to contrast this approach with the one based on diffusivity and time ACFs used in the present work. For the present systems we observe a change in the thermal expansion coefficient at a temperature of around 400 K, which would suggest much higher glass transition temperatures (Section S6). At the same time, one can observe from the analysis of the normal vector ACF that in this temperature range the relaxation time for the slowest process  $\tau_3$  reaches the limit of the MD time scale. Similar limitations of, for example, the diffusivity on MD time scales compared to experiments have also been observed for other conjugated systems.<sup>54</sup> The change in the thermal expansion is thus merely a direct result of the limited MD time scale rather than a feature of the system. As a result, at least for the present systems the analysis of the thermal

#### The Journal of Physical Chemistry B

expansion cannot be expected to yield a physically meaningful estimate of the glass transition temperature. Further comparison between the thermal expansion method and the method presented in the present work is needed to fully characterize in which situations they are applicable.

## CONCLUSIONS

The method for extending the temperature range using Bayesian regression presented in this work allows us to study relaxation processes in liquid and supercooled liquid systems containing hundreds to thousands of molecules. Hence, it is possible to make material-specific predictions for the glass transition temperature and the kinetic fragility. The general approach is directly extendable to other systems, where especially the diffusivity can be readily computed. This work serves as a first step toward accurately describing the complex relaxation processes in multicomponent mixtures of perylene derivatives. Insight into these relaxation processes is key in obtaining a systematic understanding of the dynamics of perylene derivatives, enabling the design of stronger and more stable glass forming system.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.5c00837.

Calculation of the normal vector autocorrelation function; extracting diffusivity from the mean-squared displacement; details on Bayesian fitting; calculated autocorrelation functions for all perylene derivatives studied in this work; decomposing the autocorrelation function using Fourier filtering; supplementary video of the dynamics from decomposing the autocorrelation function; estimating glass transition tempeatures from simulated annealing; and traces and corner plots from MCMC sampling (PDF)

Movie: Relaxation process separation (GIF)

#### AUTHOR INFORMATION

#### **Corresponding Author**

Paul Erhart – Department of Physics, Chalmers University of Technology, Gothenburg SE-41296, Sweden; orcid.org/ 0000-0002-2516-6061; Email: erhart@chalmers.se

#### Authors

- Eric Lindgren Department of Physics, Chalmers University of Technology, Gothenburg SE-41296, Sweden; Orcid.org/ 0000-0002-8549-6839
- Jan Swenson Department of Physics, Chalmers University of Technology, Gothenburg SE-41296, Sweden; orcid.org/ 0000-0001-5640-4766
- Christian Müller Department of Chemistry and Chemical Engineering, Chalmers University of Technology, Gothenburg SE-41296, Sweden; orcid.org/0000-0001-7859-7909

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcb.5c00837

#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We are grateful to Göran Wahnström for helpful discussions. This work was funded by the Swedish Foundation for Strategic Research via the SwedNESS graduate school (GSn15-0008), the Swedish Research Council (grant numbers 2019-04020, 2020-04935, 2021-05072, 2022-02977), and the Chalmers Initiative for Advancement of Neutron and Synchrotron Techniques. The computations were enabled by resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS) at C3SE, NSC, and PDC partially funded by the Swedish Research Council through grant agreements no. 2022-06725 and no. 2018-05973.

#### REFERENCES

(1) Zhang, G.; Lin, F. R.; Qi, F.; Heumüller, T.; Distler, A.; Egelhaaf, H.-J.; Li, N.; Chow, P. C. Y.; Brabec, C. J.; Jen, A. K.-Y.; et al. Renewed Prospects for Organic Photovoltaics. *Chem. Rev.* **2022**, *122*, 14180–14274.

(2) Zhu, L.; Zhang, M.; Zhou, Z.; Zhong, W.; Hao, T.; Xu, S.; Zeng, R.; Zhuang, J.; Xue, X.; Jing, H.; et al. Progress of Organic Photovoltaics towards 20% Efficiency. *Nature Reviews Electrical Engineering* **2024**, *1*, 581–596.

(3) Hou, J.; Inganäs, O.; Friend, R. H.; Gao, F. Organic Solar Cells Based on Non-Fullerene Acceptors. *Nat. Mater.* **2018**, *17*, 119–128.

(4) Tang, H.; Liao, Z.; Chen, Q.; Xu, H.; Huang, J.; Han, J.; Hu, D.; Luo, Y.; Lu, S.; Baran, D.; et al. Elucidating the Optimal Material Combinations of Organic Photovoltaics for Maximum Industrial Viability. *Joule* **2024**, *8*, 2208–2219.

(5) Snyder, C. R.; DeLongchamp, D. M. Glassy Phases in Organic Semiconductors. *Curr. Opin. Solid State Mater. Sci.* **2018**, *22*, 41–48. (6) Ha, J. M.; Hur, S. H.; Pathak, A.; Jeong, J.-E.; Woo, H. Y. Recent

Advances in Organic Luminescent Materials with Narrowband Emission. NPG Asia Mater. 2021, 13, 53.

(7) Chiba, T.; Pu, Y.-J.; Kido, J.*Handbook of Organic Light-Emitting Diodes*; Adachi, C.; Hattori, R.; Kaji, H.; Tsujimura, T., Eds.; Springer Japan: Tokyo, 2018; pp 1–22.

(8) Salthouse, R. J.; Moth-Poulsen, K. Multichromophoric Photoswitches for Solar Energy Storage: From Azobenzene to Norbornadiene, and MOST Things in Between. *Journal of Materials Chemistry A* **2024**, *12*, 3180–3208.

(9) Wang, Z.; Hölzel, H.; Moth-Poulsen, K. Status and Challenges for Molecular Solar Thermal Energy Storage System Based Devices. *Chem. Soc. Rev.* **2022**, *51*, 7313–7326.

(10) Uji, M.; Zähringer, T. J. B.; Kerzig, C.; Yanai, N. Visible-to-UV Photon Upconversion: Recent Progress in New Materials and Applications. *Angew. Chem., Int. Ed.* **2023**, *62*, No. e202301506.

(11) Müller, C. On the Glass Transition of Polymer Semiconductors and Its Impact on Polymer Solar Cell Stability. *Chem. Mater.* **2015**, *27*, 2740–2754.

(12) Hultmark, S.; Cravcenco, A.; Kushwaha, K.; Mallick, S.; Erhart, P.; Börjesson, K.; Müller, C. Vitrification of Octonary Perylene Mixtures with Ultralow Fragility. *Sci. Adv.* **2021**, *7*, No. eabi4659.

(13) Paleti, S. H. K.; et al. Hexanary Blends: A Strategy towards Thermally Stable Organic Photovoltaics. *Nat. Commun.* **2023**, *14*, 4608.

(14) Wahnström, G. Molecular-Dynamics Study of a Supercooled Two-Component Lennard-Jones System. *Phys. Rev. A* 1991, 44, 3752–3764.

(15) Lewis, L. J.; Wahnström, G. Relaxation of a Molecular Glass at Intermediate Times. *Solid State Commun.* **1993**, *86*, 295–299.

(16) Callaway, C. P.; Bombile, J. H.; Mask, W.; Ryno, S. M.; Risko, C. Thermomechanical Enhancement of DPP-4T through Purposeful  $\pi$ -Conjugation Disruption. J. Polym. Sci. **2022**, 60, 559–568.

(17) Frenkel, D.; Smit, B. Understanding Molecular Simulation, 2nd edition; Academic Press, Inc.: USA, 2001.

(18) Abraham, M. J.; Murtola, T.; Schulz, R.; Páll, S.; Smith, J. C.; Hess, B.; Lindahl, E. GROMACS: High Performance Molecular Simulations through Multi-Level Parallelism from Laptops to Supercomputers. *SoftwareX* 2015, 1–2, 19–25.

(19) Jorgensen, W. L.; Tirado-Rives, J. The OPLS [Optimized Potentials for Liquid Simulations] Potential Functions for Proteins, Energy Minimizations for Crystals of Cyclic Peptides and Crambin. J. Am. Chem. Soc. **1988**, 110, 1657–1666.

(20) Jorgensen, W. L.; Tirado-Rives, J. Potential Energy Functions for Atomic-Level Simulations of Water and Organic and Biomolecular Systems. *Proc. Natl. Acad. Sci. U. S. A.* **2005**, *102*, 6665–6670.

(21) Dodda, L. S.; Vilseck, J. Z.; Tirado-Rives, J.; Jorgensen, W. L. 1.14\*CM1A-LBCC: Localized Bond-Charge Corrected CM1A Charges for Condensed-Phase Simulations. *J. Phys. Chem. B* 2017, 121, 3864–3870.

(22) Dodda, L. S.; Cabeza de Vaca, I.; Tirado-Rives, J.; Jorgensen, W. L. LigParGen Web Server: An Automatic OPLS-AA Parameter Generator for Organic Ligands. *Nucleic Acids Res.* **2017**, *45*, W331–W336.

(23) Malde, A. K.; Zuo, L.; Breeze, M.; Stroet, M.; Poger, D.; Nair, P. C.; Oostenbrink, C.; Mark, A. E. An Automated Force Field Topology Builder (ATB) and Repository: Version 1.0. *J. Chem. Theory Comput.* **2011**, *7*, 4026–4037.

(24) Canzar, S.; El-Kebir, M.; Pool, R.; Elbassioni, K.; Malde, A. K.; Mark, A. E.; Geerke, D. P.; Stougie, L.; Klau, G. W. Charge Group Partitioning in Biomolecular Simulation. *Journal of Computational Biology* **2013**, *20*, 188–198.

(25) Koziara, K. B.; Stroet, M.; Malde, A. K.; Mark, A. E. Testing and Validation of the Automated Topology Builder (ATB) Version 2.0: Prediction of Hydration Free Enthalpies. *Journal of Computer-Aided Molecular Design* **2014**, *28*, 221–233.

(26) Hess, B.; Bekker, H.; Berendsen, H. J. C.; Fraaije, J. G. E. M. LINCS: A Linear Constraint Solver for Molecular Simulations. *J. Comput. Chem.* **1997**, *18*, 1463–1472.

(27) Berendsen, H. J. C.; Postma, J. P. M.; van Gunsteren, W. F.; DiNola, A.; Haak, J. R. Molecular Dynamics with Coupling to an External Bath. J. Chem. Phys. **1984**, *81*, 3684–3690.

(28) Bussi, G.; Donadio, D.; Parrinello, M. Canonical Sampling through Velocity Rescaling. J. Chem. Phys. 2007, 126, No. 014101.
(29) McGibbon, R. T.; Beauchamp, K. A.; Harrigan, M. P.; Klein,

C.; Swails, J. M.; Hernández, C. X.; Schwantes, C. R.; Wang, L.-P.; Lane, T. J.; Pande, V. S. MDTraj: A Modern Open Library for the Analysis of Molecular Dynamics Trajectories. *Biophys. J.* **2015**, *109*, 1528–1532.

(30) Harris, C. R.; et al. Array Programming with NumPy. *Nature* 2020, 585, 357–362.

(31) McKinney, W. Data Structures for Statistical Computing in Python; scipy, 2010.

(32) The pandas development team Pandas-Dev/Pandas: Pandas. Zenodo, 2023. https://zenodo.org/records/8092754 (accessed April 2025).

(33) Virtanen, P.; et al. SciPy 1.0: Fundamental Algorithms for Scientific Computing in Python. *Nat. Methods* **2020**, *17*, 261–272.

(34) Foreman-Mackey, D.; Hogg, D. W.; Lang, D.; Goodman, J. Emcee: The MCMC Hammer. *Publications of the Astronomical Society of the Pacific* **2013**, *125*, 306.

(35) Hunter, J. D. Matplotlib: A 2D Graphics Environment. *Computing in Science & Engineering* **2007**, *9*, 90–95.

(36) Waskom, M. L. Seaborn: Statistical Data Visualization. Journal of Open Source Software **2021**, 6, 3021.

(37) Foreman-Mackey, D. Corner.Py: Scatterplot Matrices in Python. *Journal of Open Source Software* **2016**, *1*, 24.

(38) Ulmestrand, M. *Perfect-Cmaps*. 2025. https://github.com/m-ulmestrand/perfect-cmaps (accessed April 2025).

(39) Stukowski, A. Visualization and Analysis of Atomistic Simulation Data with OVITO-the Open Visualization Tool. *Modell. Simul. Mater. Sci. Eng.* **2010**, *18*, No. 015012.

(40) Rault, J. Origin of the Vogel–Fulcher–Tammann Law in Glass-Forming Materials: The  $\alpha$ - $\beta$  Bifurcation. J. Non-Cryst. Solids 2000, 271, 177–217.

(41) Pipertzis, A.; Abdou, N.; Xu, J.; Asp, L. E.; Martinelli, A.; Swenson, J. Ion Transport, Mechanical Properties and Relaxation Dynamics in Structural Battery Electrolytes Consisting of an Imidazolium Protic Ionic Liquid Confined into a Methacrylate Polymer. *Energy Mater.* **2023**, *3*, 300050.

(42) Ngai, K. L.; Floudas, G.; Plazek, D. J.; Rizos, A. K. Encyclopedia of Polymer Science and Technology; John Wiley & Sons, Ltd, 2002.

(43) Lewis, L. J.; Wahnström, G. Molecular-Dynamics Study of Supercooled Ortho-Terphenyl. *Phys. Rev. E* 1994, *50*, 3865–3877.

(44) Saiter, A.; Saiter, J. M.; Grenet, J. Cooperative Rearranging Regions in Polymeric Materials: Relationship with the Fragility of Glass-Forming Liquids. *Eur. Polym. J.* **2006**, *42*, 213–219.

(45) Mauro, J. C.; Yue, Y.; Ellison, A. J.; Gupta, P. K.; Allan, D. C. Viscosity of Glass-Forming Liquids. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 19780–19784.

(46) Janssen, L. M. C. Mode-Coupling Theory of the Glass Transition: A Primer. *Front. Phys.* **2018**, *6*, 97.

(47) Berthier, L.; Reichman, D. R. Modern Computational Studies of the Glass Transition. *Nature Reviews Physics* **2023**, *5*, 102–116.

(48) Patrone, P. N.; Dienstfrey, A.; Browning, A. R.; Tucker, S.; Christensen, S. Uncertainty Quantification in Molecular Dynamics Studies of the Glass Transition Temperature. *Polymer* **2016**, *87*, 246–259.

(49) Reisjalali, M.; Burgos-Mármol, J.; Manurung, R.; Troisi, A. Local Structuring of Diketopyrrolopyrrole (DPP)-Based Oligomers from Molecular Dynamics Simulations. *Phys. Chem. Chem. Phys.* **2021**, 23, 19693–19707.

(50) Farzi, N.; Ebrahim, M. Mechanical Properties and Glass Transition Temperature of Metal-Organic Framework-Filled Epoxy Resin: A Molecular Dynamics Study. *Mater. Chem. Phys.* **2024**, *314*, No. 128874.

(51) Marchin, N.; Urata, S.; Du, J. Effect of Three-Body Interaction on Structural Features of Phosphate Glasses from Molecular Dynamics Simulations. J. Chem. Phys. **2024**, 161, 154507.

(52) Lin, K.-H.; Paterson, L.; May, F.; Andrienko, D. Glass Transition Temperature Prediction of Disordered Molecular Solids. *npj Comput. Mater.* **2021**, *7*, 17.

(53) Root, S. E.; Savagatrup, S.; Pais, C. J.; Arya, G.; Lipomi, D. J. Predicting the Mechanical Properties of Organic Semiconductors Using Coarse-Grained Molecular Dynamics Simulations. *Macromolecules* **2016**, *49*, 2886–2894.

(54) Alesadi, A.; Cao, Z.; Li, Z.; Zhang, S.; Zhao, H.; Gu, X.; Xia, W. Machine Learning Prediction of Glass Transition Temperature of Conjugated Polymers from Chemical Structure. *Cell Reports Physical Science* **2022**, *3*, No. 100911.

# Supporting Information

# Probing Glass Formation in Perylene Derivatives via Atomic Scale Simulations and Bayesian Regression

Eric Lindgren<sup>1</sup>, Jan Swenson<sup>1</sup>, Christian Müller<sup>2</sup>, and Paul Erhart<sup>1,\*</sup>

<sup>1</sup> Department of Physics, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden

<sup>1</sup> Department of Chemistry and Chemical Technology, Chalmers University of Technology, SE-412 96 Gothenburg, Sweden

\* erhart@chalmers.se

# Contents

S1 Computing the normal vector autocorrelation function	$\mathbf{S2}$
S2 Extracting the diffusivity from the mean-squared displacement	$\mathbf{S2}$
<ul> <li>S3 Bayesian fitting</li> <li>S3.1 Fitting the autocorrelation function to triple exponential</li></ul>	<b>S4</b> S4 S5
S4 Autocorrelation functions for all perylene derivatives	$\mathbf{S6}$
S5 Decomposing the autocorrelation function	$\mathbf{S7}$
S6 Estimating the glass transition temperature from simulated annealing	$\mathbf{S7}$
S7 MCMC sampling         S7.1 MCMC traces: Fitting the diffusivity	<b>S7</b> <b>S7</b> <b>S8</b> <b>S9</b> <b>S10</b>
<ul> <li>S8 Corner plots</li> <li>S8.1 Corner plots: Fitting the diffusivity</li></ul>	<b>S11</b> S11 S12 S13 S14
References	<b>S16</b>



Figure S1: Schematic representation of the normal vector autocorrelation function  $J(\tau)$ , see Eq. (S3).

# S1 Computing the normal vector autocorrelation function

Given  $\mathbf{r}_i^m(t)$  as the position of atom m in molecule i at time t, the centroid position of molecule i with M atoms is defined as

$$\mathbf{r}_{i}(t) = \frac{1}{M} \sum_{m=1}^{M} \mathbf{r}_{i}^{m}(t).$$
 (S1)

We can now define the normal vector correlation function,

$$C_{\hat{n}\hat{n}}(r,\tau) = \left\langle \sum_{i=1}^{N} \sum_{j=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_{ij}) \hat{\boldsymbol{n}}_{i}(t) \cdot \hat{\boldsymbol{n}}_{j}(t+\tau) \right\rangle_{t},$$
(S2)

where  $\hat{\boldsymbol{n}}_i(t)$  is the normal vector of molecule *i*, and is calculated by computing the normal to the point cloud of atoms in the molecule,  $\{\boldsymbol{r}_i^m(t)\}$ . The ensemble average is taken over all frames in the trajectory. In particular, we study the special case of the normal vector autocorrelation function  $C_{\hat{n}\hat{n}}(0,\tau)$ , denoted  $J(\tau)$ .

$$J(\tau) = C_{\hat{n}\hat{n}}(\tau) = \left\langle \hat{\boldsymbol{n}}_i(t) \cdot \hat{\boldsymbol{n}}_i(t+\tau) \right\rangle_{it}, \qquad (S3)$$

with the ensemble average taken over all frames t and each molecule i in the system. Equation (S3) can be efficiently computed from the signal  $\hat{n}_i(t)$  using the Wiener-Kinchin theorem.

We may also extract the standard error as an uncertainty estimate for  $J(\tau)$  from the correlation function for each molecule  $J_i(\tau)$  before computing the ensemble average in equation Eq. S3, using the central limit theorem,

$$\sigma_J(\tau) = \sqrt{\operatorname{Var}\left(\{J_i\}_{i=1}^N\right)} / \sqrt{N},\tag{S4}$$

where N is the number of molecules in the system. The normal vector  $\hat{n}_i(t)$  and  $J(\tau)$  are schematically represented in Fig. S1.

Two production molecular dynamics (MD) simulations, with a length of 100 ps and 10 ns respectively, were run in order to get the same number of statistics for short and long time lags. The trajectory files were written every 1 fs for the 100 ps simulation and every 100 fs for the 10 ns simulation. The normal vector autocorrelation functions (ACFs) according to Eq. S3 were calculated for both production runs and then spliced together at a time lag of  $\tau = 1$  ps. This splicing was also done for the standard error in equation Eq. S4.

# S2 Extracting the diffusivity from the mean-squared displacement

We obtained the molecular diffusivity D for each perylene derivative **I**–**V** and temperature, from the mean squared displacement (MSD)  $\langle \Delta r^2 \rangle$  of the molecular centroid positions<sup>1</sup>,

$$\left\langle \Delta r^2 \right\rangle = 6D\tau. \tag{S5}$$

The diffusivity was computed using production runs with a duration of up to 10 ns. D was extracted by performing a linear fit using Bayesian regression to the MSD (Fig. S2). Note that D for



Figure S2: Diffusivity computed from the MSD for each perylene derivative I-V



Figure S3: a) Mean-squared displacement and b) diffusivity obtained from the MSD measured over 100 ns MD simulations, as a function of temperature for perylene derivative **I**. Note that the diffusivity exhibits a discontinuity at 400 K, which is due to the diffusion processes reaching the timescale of the MD simulation.

high temperatures change slope; this is due to some of the derivatives transitioning to a gaseous phase. When fitting the Vogel-Fulcher-Tammann (VFT) equation we thus only considered D for temperatures < 700 K.

The lower bound in temperature for the diffusivity calculations was 400 K, due to the diffusion processes slowing down to the timescale of the MD simulation at this temperature. To demonstrate this effect, we performed a set of 100 ns MD simulations for perylene derivative I for a broad range of temperatures, and calculated the diffusivity (Fig. S3). Specifically, for perylene derivative I at 400 K, the diffusivity is  $1 \times 10^{-6}$  nm ps<sup>-1</sup>. Over the course of a 100 ns MD simulation, this means that on average each perylene molecule moves a distance of  $\approx 3$  Å. This distance is comparable to the nearest-neighbor distance between molecules, which means that at 400 K a perylene molecules barely has time to move out of the shell formed by it's neighbors.

For temperatures lower than 400 K the diffusivity decreases further, and the average distance that a perylene molecule moves becomes smaller than the nearest neighbor distance. This means that on the timescale of the MD simulation, the molecules will appear to be locked in their nearestneighbor cages, and we can no longer reliable estimate the diffusivity. We can approximate the lowest diffusivity we can estimate based on the MD simulation time using the nearest-neighbor distance. Assuming a nearest-neighbor distance of R, we require that  $\langle \Delta r^2 \rangle > R^2$ . This implies  $R^2 > 6DT$  where T is the total simulation time, from Eq. S5. By assuming a nearest neighbor distance R of 3Å and a simulation time T of 100 ns, we obtain  $D \gtrsim 10^{-13} \text{ m}^2 \text{ s}^{-1}$ . If the diffusivity drops below this threshold it can no longer be reliably estimated, which for the present system occurs at approximately 400 K.

# S3 Bayesian fitting

In this work, we use a Gaussian likelihood function, which under the assumption of independent and identically distributed  $N_d$  data  $d_i \in \mathcal{D}$ , here takes the form,

$$p(\mathcal{D}|\boldsymbol{\theta}, \mathcal{I}) = \prod_{i=1}^{N_d} \frac{1}{\sqrt{2\pi\sigma_i^2}} e^{-(M(\boldsymbol{\theta}) - d_i)^2 / (2\sigma_i^2)},$$
(S6)

with  $\sigma_i^2$  as the variance of the residual for datum  $d_i$ . We use  $\sigma_i$  to encode the standard error of the diffusivity and the ACF, as well as to perform error propagation.

## S3.1 Fitting the autocorrelation function to triple exponential

Let  $J(\tau)_T$  denote the ACF for temperature T. For each perylene derivative a–e, we have a data set of ACFs  $\mathcal{D} = \{J(\tau)_{T_i}\}_{i=1}^L$ , where L is the number of distinct temperatures studied for this derivative. In this stage, we used a Gaussian likelihood on the form in equation Eq. S6, where we let  $\sigma_i = \sigma/\sigma_{J(\tau)_{T_i}}$ , with  $\sigma_{J(\tau)_{T_i}}$  being the standard error for ACF  $J(\tau)_{T_i}$  at temperature  $T_i$ , and  $\sigma$ is a free parameter. This is a heteroscedastic error model, in which each datum has an individual error. In total, the set of free parameters to optimise in this stage was  $\boldsymbol{\theta} = \{A_1, A_2, \tau_1, \tau_2, \tau_3, \beta, \sigma\}$ .

The priors for each of the parameters were set as follows,

$$p(A_i|\mathcal{I}) = \frac{1}{0.2} e^{-|A_i/0.1|}, \text{ for } A_1, A_2$$
 (S7)

$$p(\tau_1|\mathcal{I}) = \frac{\sqrt{2}}{5\sqrt{\pi}} e^{-(\tau_1/5)^2/2}, x > 0$$
(S8)

$$p(\tau_2|\mathcal{I}) = \frac{1}{50\sqrt{2\pi}} e^{-((\tau_2 - 10)/50)^2/2}$$
(S9)

$$p(\tau_3|\mathcal{I}) = \frac{1}{\sqrt{2\pi}} e^{-(\log_{10}(\tau_3) - 3)^2/2}$$
(S10)

$$p(\beta|\mathcal{I}) = \frac{\sqrt{2}}{0.1\sqrt{\pi}} e^{-((x-1)/0.1)^2/2}, x = 2 - \beta$$
(S11)

$$p(\sigma|\mathcal{I}) = \frac{\sqrt{2}}{\sqrt{\pi}} e^{-\sigma^2/2}, x > 0 \tag{S12}$$

with the same priors being used for all temperatures. Note that the prior for  $\tau_3$  is for  $\log_{10}(\tau_3)$ , due to  $\tau_3$  spanning several orders of magnitude throughout the temperature range. The joint prior then becomes

$$p(\boldsymbol{\theta}|\mathcal{I}) = p(A_1|\mathcal{I})p(A_2|\mathcal{I})$$

$$p(\tau_1|\mathcal{I})p(\tau_2|\mathcal{I})p(\tau_3|\mathcal{I})$$

$$p(\beta|\mathcal{I})p(\sigma|\mathcal{I}).$$
(S13)

We then used Markov-chain Monte Carlo (MCMC) sampling to sample the posterior  $p(\theta|\mathcal{D},\mathcal{I})$ . For numerical stability, the likelihood and priors were rewritten as the log-likelihood and logprior respectively. Optimizing the posterior or the log-posterior does not change the resulting distributions, and thus the quantity that was optimized was, up to a constant,

$$\ln\left(p(\boldsymbol{\theta}|\mathcal{D},\mathcal{I},T)\right) = \ln\left(p(\mathcal{D}|\boldsymbol{\theta},\mathcal{I},T)\right) + \ln\left(p(\boldsymbol{\theta}|\mathcal{I})\right).$$
(S14)

See Sect. S7 and Sect. S8 in the Supplementary Information for traces and corner plots resulting from the Bayesian fitting procedure.

$$J(\tau) = A_1 e^{-\tau/\tau_1} + A_2 e^{-\tau/\tau_2} + (1 - A_1 - A_2) e^{(-\tau/\tau_3)^{\beta}},$$
(S15)

The triple-exponential model in equation Eq. S15 has six free parameters, and combined with the noise parameter  $\sigma$  we thus obtain a seven-dimensional posterior distribution  $p(\theta | \mathcal{D}, \mathcal{I}, T)$ . From the posterior distribution, the marginal distribution for  $\tau_3$  can then be extracted,

$$p(\tau_3|\mathcal{D},\mathcal{I},T) \propto \int p(\boldsymbol{\theta}|\mathcal{D},\mathcal{I},T) dA_1 dA_2 d\tau_1 d\tau_2 d\beta d\sigma.$$
 (S16)

Computationally, the marginal distribution can be extracted by only studying the samples distributions for the marginal parameters of interest. Mean  $\mu_{\tau_3}(T)$  and standard deviation  $\sigma_{\tau_3}(T)$  of  $\tau_3(T)$  were then extracted from  $p(\tau_3|\mathcal{D},\mathcal{I},T)$  in order to inform the second stage of the regression process.

#### S3.2 Fitting the diffusivity and autocorrelation to the VFT equation

Both the diffusivity and  $\tau_3$  were fit to a VFT equation using the same framework, as described in this section. The only difference between the two is the sign in the exponential of the VFT equation, which was negative for the diffusivity since the diffusivity decreases with temperature. We present the fitting for  $\tau_3$  here as an example.

We fitted a VFT equation the mean values  $\tau_3(T)$ ,  $\mu_{\tau_3}(T)$ , from the first stage of the process,

$$K(T; \boldsymbol{\theta'}) = \tau_3^0 \exp \frac{B}{k_B (T - T_{\rm VF})},\tag{S17}$$

where  $k_B$  is the Boltzmann constant. The VFT equation is an experimentally observed law that the non-Arrhenius behavior of  $\alpha$ -relaxation in glass forming systems obeys, where  $\tau_3^0$ , B, and  $T_{\rm VF}$ are empirical fitting parameters<sup>2</sup>.

Note that the VFT equation as written in the main paper does not include  $k_B$ , and is instead written on the common form  $K(T; \theta') = \tau_3^0 \exp \frac{B}{(T-T_{\rm VF})}$  However, when actually fitting the VFT equation we introduced  $k_B$  for numerical reasons as this yields a value of  $B \leq 1$ .  $k_B$  was then absorbed back into B for all subsequent calculations of  $T_a$ , m etc.

absorbed back into *B* for all subsequent calculations of  $T_g$ , *m* etc. The data set consisted of  $\mathcal{D}' = \{\mu_{\tau_3}(T_i)\}_{i=1}^L$ . In this case also a Gaussian likelihood with heteroscedastic errors  $\sigma_i = \sigma'/\sigma_{\tau_3}(T)$  was used, with  $\sigma_{\tau_3}(T)$  as the estimated standard deviation of the posterior distribution for  $\tau_3$ . In total, four free parameters were fitted at this stage,  $\theta' = \{\tau_3^0, B, T_{\rm VF}, \sigma'\}$ .

The priors used in the second stage of the fitting procedure were,

$$p(\tau_3^0|\mathcal{I}) = \frac{\sqrt{2}}{\sqrt{\pi}} e^{-(\tau_3^0)^2/2}, x > 0$$
(S18)

$$p(B|\mathcal{I}) = \frac{\sqrt{2}}{\sqrt{\pi}} e^{-B^2/2}, x > 0$$
(S19)

$$p(T_{\rm VF}|\mathcal{I}) = \frac{1}{200\sqrt{2}\pi} e^{-(T_{\rm VF} - 200)/200)^2/2}$$
(S20)

$$p(\sigma'|\mathcal{I}) = \frac{\sqrt{2}}{\sqrt{\pi}} e^{-\sigma'^2/2}, x > 0$$
(S21)

The log-posterior was then optimized using MCMC-sampling, similarly to the first stage of the regression process. See Sect. S7 and Sect. S8 in the Supplementary Information for all traces and corner plots resulting from the Bayesian fitting procedure.

The resulting posterior distribution  $p(\theta'|D', \mathcal{I}')$  of the fit to the VFT equation was then used to extrapolate  $\tau_3$  to lower temperatures, feeding the posterior distribution samples through the model in equation Eq. S17. The glass transition temperature  $T_g$  is roughly taken to be the temperature at which the slowest relaxation process in the system exceeds  $100 \, \mathrm{s}^2$ . We therefore took the temperature at which  $\tau_3(T)$  exceeded 100 s for each sample of the posterior distribution as an individual estimate of  $T_g$ . In total, for each molecule a–e, we obtained a distribution  $p(T_g|\mathcal{D}, \mathcal{D}', \mathcal{I})$ of estimates of the glass transition temperature  $T_g$ . Note that the estimate for  $T_g$  is relatively stable with regard to the choice of cutoff time for  $\tau_3(T)$ . Decreasing the time to 1 s or increasing it to 10 000 s changes  $T_g$  by 7 K and -5 K, respectively. These changes are smaller than the standard deviation of  $p(T_g|\mathcal{D}, \mathcal{D}', \mathcal{I})$ , which typically is approximately 10 K to 20 K for the systems under study.

The glass transition temperature was similarly estimated from the diffusivity D(T) as obtained from the MSD, using the same workflow. In this case, the inverse of the diffusivity was fitted against a VFT equation. The MSD over 100s was then calculated as a function of temperature, and  $T_g$  was estimated as the temperature at which the MSD reaches 100 Å<sup>2</sup>.



# S4 Autocorrelation functions for all perylene derivatives

Figure S4: Calculated and fitted ACFs using (S15). Error bands of the fits are plus and minus one standard deviation.



Figure S5: Calculated and fitted ACFs using (S15). Error bands of the fits are plus and minus one standard deviation.



Figure S6: Calculated and fitted ACFs using (S15). Normal vector ACF for derivative IV



Figure S7: Glass transition temperature  $T_g$  estimated via simulated annealing using four different cooling rates for ethyl-perylene, a perylene derivative denoted II in this work.  $T_g$  is taken as the point at which the slope of the density changes, roughly at 412 K. This estimate from simulated annealing is severely overestimated compared to the experimentally measured glass transition temperature of 252.35 K from<sup>3</sup>. Note that the system size here is significantly larger than in the main paper, consisting of 5179 residues for a total of 217 322 atoms.

# S5 Decomposing the autocorrelation function

Let  $\{\mathbf{r}_{i}^{k}(t)\}_{k=1}^{M}$  be a trajectory of the coordinates of the atoms in a specific molecule *i*. The trajectory of a single molecule *i* was extracted and the centroid of the molecule,  $\mathbf{r}_{i}(t)$ , was placed in the middle of the simulation cell for each frame to avoid effects of the molecule moving over the periodic boundaries. The power spectrum of for each Cartesian component of the shifted trajectory was then computed, convoluted with a filter  $F(\omega)$  in the Fourier domain, and the filtered power spectrum  $S'(\omega)$  was then back transformed to yield a filtered trajectory  $\{\mathbf{r}_{i}^{\prime k}(t)\}_{k=1}^{M}$ ,

$$S_{l}(\omega) = \mathcal{F}\left[r_{il}^{k}(t)\right]^{2}(\omega), l \in \{x, y, z\}$$

$$S_{l}^{\prime}(\omega) = S_{l}(\omega) * F(\omega)$$

$$\Rightarrow r_{il}^{\prime k}(t) = \mathcal{F}^{-1}\left[S_{l}^{\prime}(\omega)\right](t)$$
(S22)

where  $\mathcal{F}$  denotes the Fourier transform. The filter  $F(\omega)$  is a simplified bandpass filter, on the form

$$F(\omega) \begin{cases} 1, & \omega_1 \le \omega \le \omega_2 \\ 0, & \text{otherwise.} \end{cases}$$
(S23)

By setting the filter frequencies  $\omega_1$  and  $\omega_2$  to match the expected time scales for  $\tau_1$ ,  $\tau_2$  and  $\tau_3$ , this scheme gives a rough decomposition into what types of motion take place on the different timescales and allows us to somewhat elucidate what processes the ACF capture. A visualization of the decomposition scheme is available in the supplementary movie, Video V1.

# S6 Estimating the glass transition temperature from simulated annealing

Here we demonstrate the use of simulated annealing for predicting the glass transition temperature of derivative II Fig. S7. Following the general approach set out in the literature,  $T_g$  is taken as the point at which the density changes slope<sup>4–9</sup>. This approach yields  $T_g$  that is overstimated by approximately 150 K, compared to experiments using differential scanning calorimetry from<sup>3</sup>.

# S7 MCMC sampling

Note that all the traces presented in this section have been sub-sampled by the maximum autocorrelation time over all chains. The traces thus only contain uncorrelated values.

## S7.1 MCMC traces: Fitting the diffusivity

In the interest of space, we only show a representative trace plot for derivative I at 450 K (Fig. S8). All traces for the remianing perylene derivatives and temperatures are similar.



Figure S8: MCMC parameter trace for fitting the diffusivity in equation (S5) to the MSD at 450 K for derivative  ${\bf I}$ 

# S7.2 MCMC traces: Fitting the VFT equation to the diffusivity



Figure S9: MCMC parameter trace for the fit of the VFT equation to the diffusivity.



Figure S10: MCMC parameter trace for the fit of the VFT equation to the diffusivity.



Figure S11: MCMC parameter trace for the fit of the VFT equation to the diffusivity for derivative  ${\bf V}$ 

# S7.3 MCMC traces: Fitting the normal vector ACF

In the interest of space, we only show a representative trace plot for derivative I at 450 K (Fig. S12). All traces for the remianing perylene derivatives and temperatures are similar.



Figure S12: MCMC parameter trace for fitting the triple exponential function in equation (S15) to the normal vector ACF at 450 K for derivative I





Figure S13: MCMC parameter trace for the fit of the VFT equation to the normal vector ACF.



Figure S14: MCMC parameter trace for the fit of the VFT equation to the normal vector ACF.



Figure S15: MCMC parameter trace for the fit of the VFT equation to the normal vector ACF for derivative  $\mathbf{V}$ .

# S8 Corner plots

Note that all the traces presented in this section have been sub-sampled by the maximum autocorrelation time over all chains. Thus, the corner plots only contain uncorrelated values.

# S8.1 Corner plots: Fitting the diffusivity

In the interest of space, we only show a representative corner plot for derivative I at 450 K (Fig. S16). All corner plots for the remianing perylene derivatives and temperatures are similar.



Figure S16: Corner plot of the MCMC parameter samples for fitting the diffusivity in equation (S5) to the MSD at 450 K for derivative I.





Figure S17: Corner plot for the fit of the VFT equation to the diffusivity.



Figure S18: Corner plot for the fit of the VFT equation to the diffusivity.



Figure S19: Corner plot for the fit of the VFT equation to the diffusivity for derivative  ${\bf V}$ 

# S8.3 Corner plots: Fitting the normal vector ACF

In the interest of space, we only show a representative corner plot for derivative I at 450 K (Fig. S20). All corner plots for the remianing perylene derivatives and temperatures are similar.



Figure S20: Corner plot of the MCMC parameter samples for fitting the triple exponential function in (S15) to the normal vector ACF at 450 K for derivative **I**.





Figure S21: Corner plot for the fit of the VFT equation to the normal vector ACF.



Figure S22: Corner plot for the fit of the VFT equation to the normal vector ACF.



Figure S23: Corner plot for the fit of the VFT equation to the normal vector ACF for derivative  $\mathbf{V}.$ 

# References

- Daan Frenkel and Berend Smit. Understanding Molecular Simulation. Academic Press, Inc., USA, 2nd edition, September 2001. ISBN 978-0-12-267351-1.
- [2] Jacques Rault. Origin of the Vogel-Fulcher-Tammann law in glass-forming materials: The α-β bifurcation. Journal of Non-Crystalline Solids, 271(3):177-217, July 2000. ISSN 0022-3093. doi: 10.1016/S0022-3093(00)00099-5. URL https://www.sciencedirect.com/science/article/ pii/S0022309300000995.
- [3] Sandra Hultmark, Alex Cravcenco, Khushbu Kushwaha, Suman Mallick, Paul Erhart, Karl Börjesson, and Christian Müller. Vitrification of octonary perylene mixtures with ultralow fragility. *Science Advances*, 7(29):eabi4659, July 2021. ISSN 2375-2548. doi: 10.1126/sciadv. abi4659. URL https://advances.sciencemag.org/lookup/doi/10.1126/sciadv.abi4659.
- [4] Nahid Farzi and Maede Ebrahim. Mechanical properties and glass transition temperature of metal-organic framework-filled epoxy resin: A molecular dynamics study. *Materi*als Chemistry and Physics, 314:128874, February 2024. ISSN 0254-0584. doi: 10.1016/j. matchemphys.2023.128874. URL https://www.sciencedirect.com/science/article/pii/ S0254058423015821.
- [5] Navid Marchin, Shingo Urata, and Jincheng Du. Effect of three-body interaction on structural features of phosphate glasses from molecular dynamics simulations. *The Journal of Chemical Physics*, 161(15):154507, October 2024. ISSN 0021-9606. doi: 10.1063/5.0225188. URL https: //doi.org/10.1063/5.0225188.
- [6] Connor P. Callaway, Joel H. Bombile, Walker Mask, Sean M. Ryno, and Chad Risko. Thermomechanical enhancement of DPP-4T through purposeful π-conjugation disruption. *Journal* of Polymer Science, 60(3):559-568, 2022. ISSN 2642-4169. doi: 10.1002/pol.20210494. URL https://onlinelibrary.wiley.com/doi/abs/10.1002/pol.20210494.
- Kun-Han Lin, Leanne Paterson, Falk May, and Denis Andrienko. Glass transition temperature prediction of disordered molecular solids. *npj Computational Materials*, 7(1):1-7, November 2021. ISSN 2057-3960. doi: 10.1038/s41524-021-00647-w. URL https://www.nature.com/articles/s41524-021-00647-w.
- [8] Paul N. Patrone, Andrew Dienstfrey, Andrea R. Browning, Samuel Tucker, and Stephen Christensen. Uncertainty quantification in molecular dynamics studies of the glass transition temperature. *Polymer*, 87:246–259, March 2016. ISSN 0032-3861. doi: 10.1016/j.polymer.2016.01.074. URL https://www.sciencedirect.com/science/article/pii/S003238611630074X.
- [9] Samuel E. Root, Suchol Savagatrup, Christopher J. Pais, Gaurav Arya, and Darren J. Lipomi. Predicting the Mechanical Properties of Organic Semiconductors Using Coarse-Grained Molecular Dynamics Simulations. *Macromolecules*, 49(7):2886–2894, April 2016. ISSN 0024-9297. doi: 10.1021/acs.macromol.6b00204. URL https://doi.org/10.1021/acs.macromol.6b00204.