Molecular dynamics study on interface morphology of vapor-deposited amorphous organic thin films

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Additional information about target molecules

Table S1 The glass transition temperatures (T_g), the molecular length, and the molecular volume of CBP, α-NPD, and BSB-Cz. $T_{g,sim}$ is the simulated glass transition temperature and T_g is experimental value. ΔT_g is the difference between simulated and experimental value. The molecular length is estimated from simulation snapshots and the molecular volume is estimated from bulk density at 450 K.

Molecule	$T_{g,sim}$ (K)	T_g (K)	ΔT_g (K)	Length (Å)	Volume (Å^3)
CBP	459	335[1]	124	18.8	730
α-NPD	473	362[2]	111	17.9	940
BSB-Cz	497	389[3]	108	30.4	1040

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Validation of frozen-bulk method

We validated that the use of frozen-bulk method has little effect on the resulting morphology. The frozen-bulk method is inspired by the fact that below the glass transition temperature, the molecules near the surface have high diffusivity, but the molecules in the bulk region barely move. Fig. S1a shows the change in the orientation order parameter ΔS during the deposition simulation against the initial distance from the free surface (for CBP

and BSB-Cz molecules). In the Fig. S1a, it can be seen that S of CBP molecules changes much below 2.5 nm depth, but it does not change substantially over 2.5 nm depth (especially at 400 and 450 K). S of BSB-Cz molecules does not change over 4 nm depth at 600 K and 2 nm depth at 450 K. Therefore, we can obtain almost same morphology if we only describe the surface region correctly. In analogy to S, we defined a parameter H as

$$H = \frac{3\left\langle \cos^2 \varphi \right\rangle - 1}{2} \, ,$$

where φ is the angle between initial and the final molecular axis. H describes how much the molecular orientation changed during the further deposition. Fig. S1c shows H against the distance from free surface at 400 K. The effect of fixed bulk in the frozen-bulk method persist about 2 nm above the fixed region. However, H is only slightly affected near the surface. It is expected from ΔS that S slightly decreases by ~0.05 and actually there is slight decrease in the S value. However, the change is marginal. We determined the distance to the frozen bulk by adding 2 nm to the thickness of surface layer that needs to be described correctly. The determined values are 4.5 nm for CBP and α-NPD, and 6 nm for BSB-Cz.
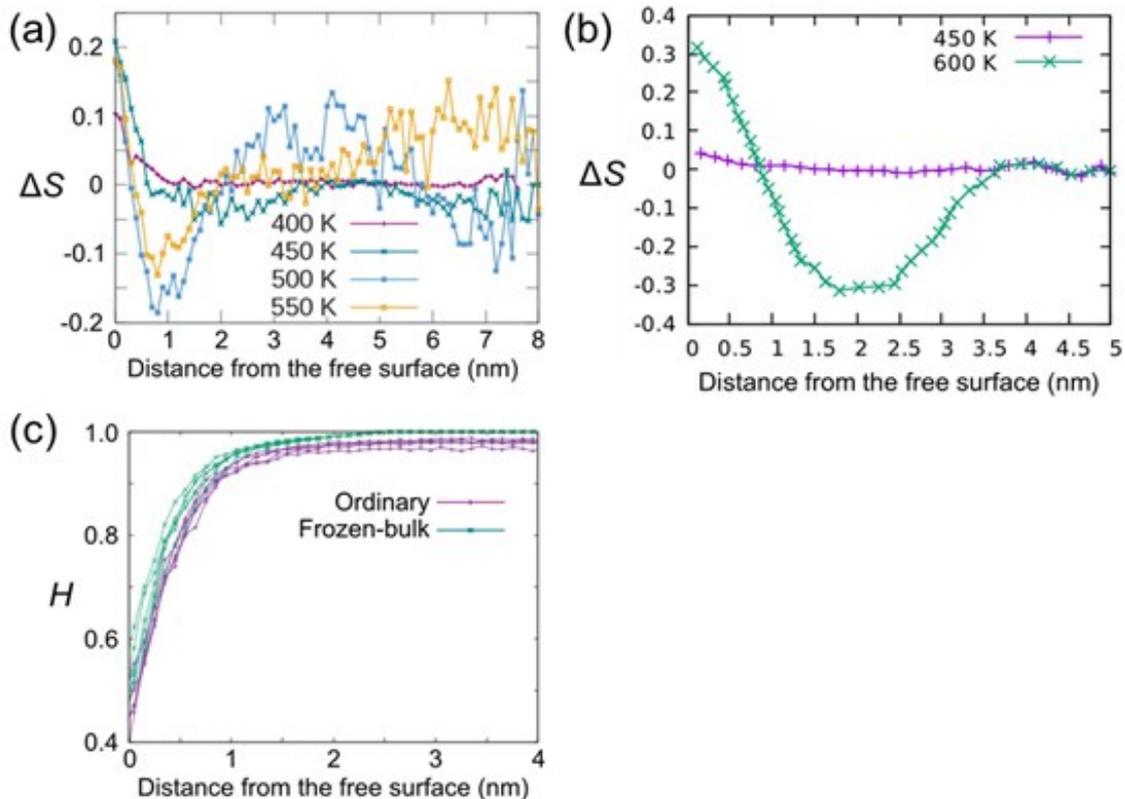
Fig. S1 the change in the orientation order parameter ΔS during the deposition simulation against the initial distance from the free surface for (a) CBP molecules and (b) BSB-Cz molecules. (c) H against the distance from the free surface for both ordinary deposition simulation and frozen-bulk method.

Influence of long-range treatment

In the deposition simulation, the cutoff distance of 10 Å is applied on Coulomb and van der Waals interactions and long-range electrostatic interactions are not treated. It is necessary to include long-range treatment in general. However, long-range treatment is not critical in our simulations because all molecules have zero dipole moment. (The quadrupole-quadrupole interaction is proportional to R^{-5}.) We have investigated the influence of long-range treatment. We applied particle-particle particle-mesh (PPPM) method with slab correction (EW3DC) which is available in LAMMPS. (The computational cost increased by ~50%.) We will refer to the method that uses cutoff distance without any long-range treatment as Cutoff.

First, we have checked the force error (the difference between Cutoff and EW3DC) for a CBP/BSB-Cz interface structure at 400 K, which might have large errors due to horizontal molecular alignment. Fig. S2 shows z-component of force error vs. z-coordinate for each atom. When comparing Cutoff of 10 Å to EW3DC, most of force errors are smaller than 0.01 eV/Å (Fig S2a), with the root-mean square error (RMSE) of 0.011 eV/ Å. Fig. S2b is the same plot but with a larger cutoff radius of 30 Å, which shows smaller errors with RMSE of 0.004 eV/Å. We note that force error is not particularly large on interface or surface. x- and y-components of force error is not shown but they are similar to z-components.
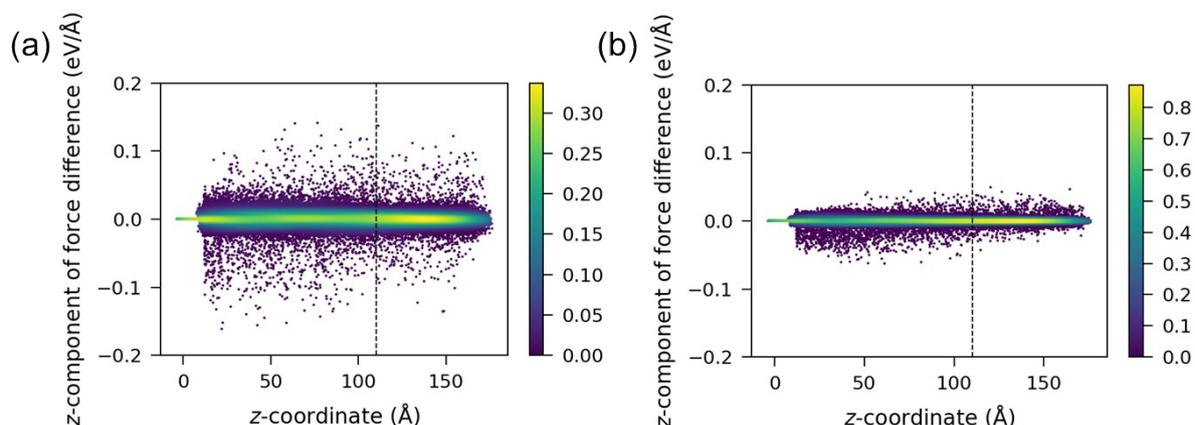
Fig. S2 *z*-component of force difference vs. *z*-coordinate for (a) cutoff of 10 Å without long-range treatment vs. EW3DC and (b) cutoff of 30 Å without long-range treatment vs. EW3DC. The vertical dashed line shows the position of CBP/BSB-Cz interface, and the color indicates the density of points.

In order to examine how the simulation is affected by the long-range treatment, we have estimated the glass transition temperature of CBP with melt-quench simulation using both methods, i.e, 10-Å cutoff and EW3DC. It is seen that the glass transition temperatures from Cutoff and EW3DC were almost identical.
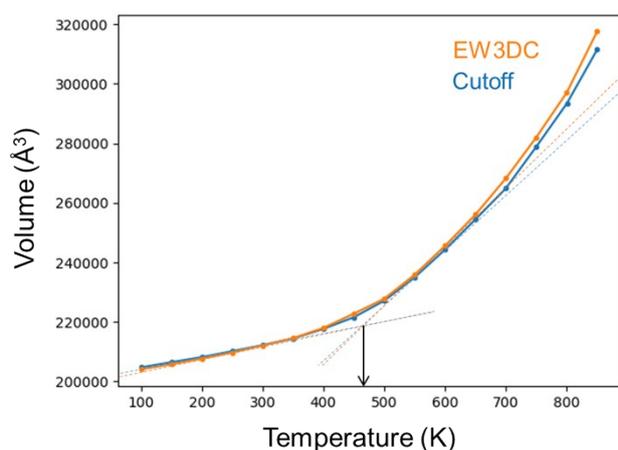

Fig. S3 Volume vs. temperature during melt-quench simulation.

Finally, we have performed deposition simulation of CBP film at 450 K (with EW3DC) to show the influence of long-range treatment on the structure of deposited films. Fig. S4 shows *H* (which is defined in "Validation of frozen-bulk method" section above) and the orientation order parameter *S* against the distance from the free surface. In Fig S4a, EW3DC(450 K) is slightly lower than Cutoff(450 K), which indicates that the diffusivity was slightly increased when long-range treatment was applied. However, the orientation order parameter *S* remained almost same as can be seen in Fig S4b. (The data points that are far away from the surface have low number of samples and may fluctuate.) Additionally, the density of deposited film decreased only slightly (by 1.5%).
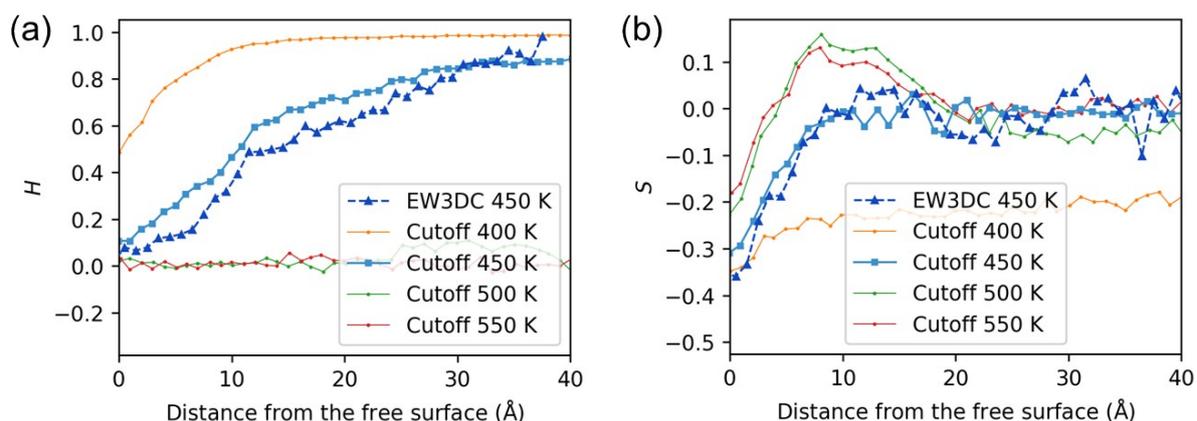
Fig. S4 (a) *H* and (b) the orientation order parameter *S* vs. the distance from the free surface.

Above results suggest that the influence of long-range treatment on *S* or T_g is negligible for the systems investigated in this study. The long-range treatment would not largely change diffusion-related properties (the degree of interdiffusion and interface thickness), because the diffusivity has only slightly increased. The long-range treatment would become crucial when molecules have permanent dipole moment.

The influence of equilibration step after reconstruction

After the deposition simulation using frozen-bulk method is finished, the final structure is reconstructed by attaching the removed parts to the final snapshot. After the reconstruction, we performed the equilibration step for 500 ps on a BSB-Cz/CBP interface at 450 K. As shown in the Fig. S5, the energy fluctuates within 0.08 kcal/mol/atom, no significant change in the morphology (such as interface thickness, molecular orientation, interdiffused volume) was observed during the equilibration. In detail, the change in the number of molecules in each region was mostly below 3%. The number of interdiffused CBP molecules remained to be the same and the number of interdiffused BSB-Cz molecules changed from 8 to 9. The change of S value of BSB-Cz for each region was below 0.023 and that for CBP was below 0.040. The overall volume increased about 2%.
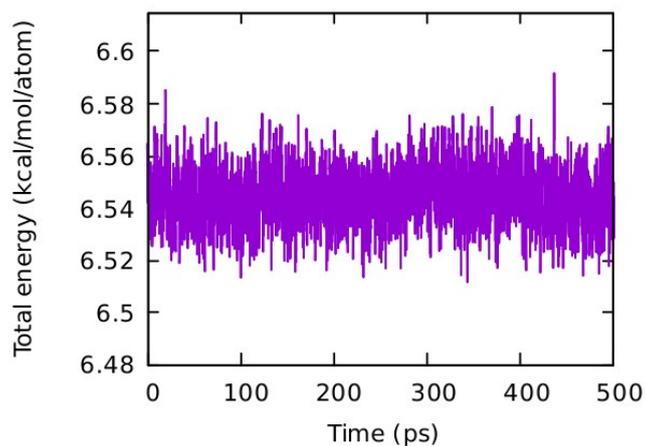
Fig. S5 The total energy per atom of BSB-Cz/CBP interface at 450 K during the equilibration step.

Density profile along z-axis

In plane-average method, the interface thickness is determined as a distance between *xy*-planes where the density of each component drops to 90% of their bulk density as shown in Fig. S6. It is seen from Table S2 that the interface thickness is overestimated by maximum 47% when plane-average method is used (compared to the new method). On the other hand, the new method is not affected by roughness and gives reliable results.

Neither reduction nor increase in the total density profile was observed in the interface, which suggests that the molecular packing in the interface is more or less the same as that of bulk. Also, we can observe a long tail in upward-diffusion, which indicates that the interface morphology is asymmetric.
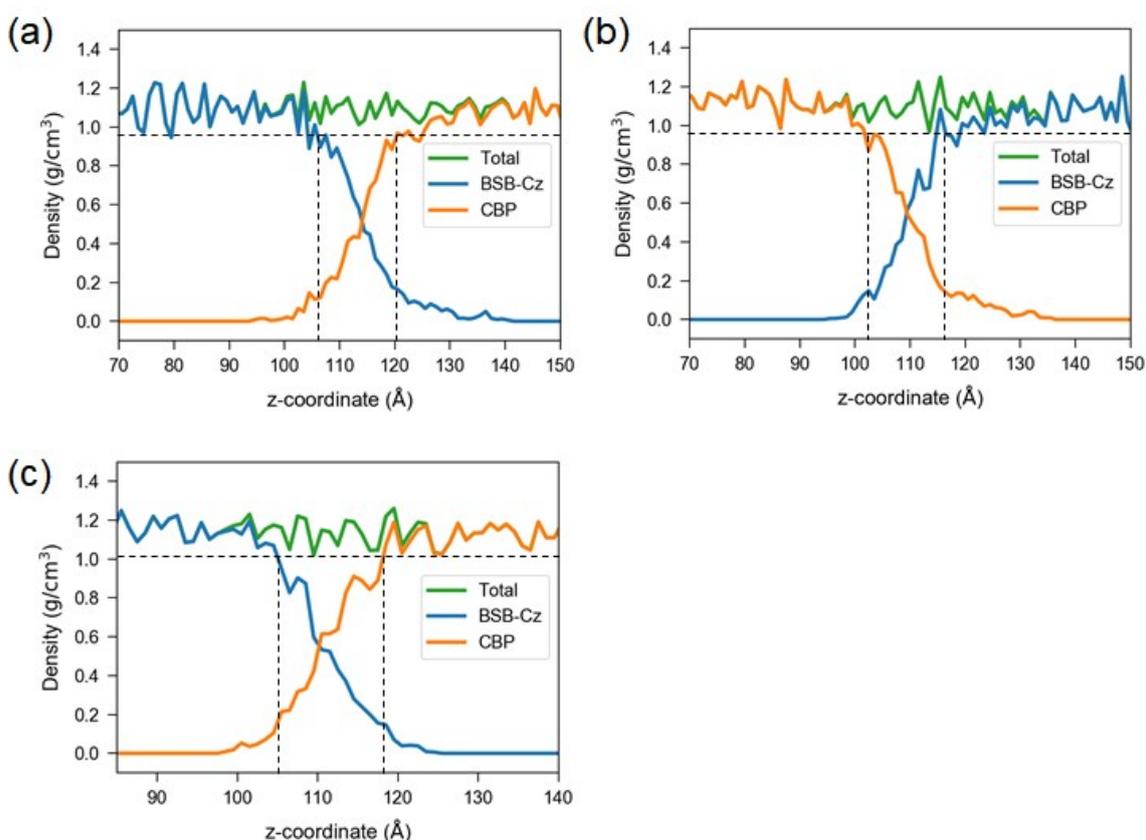
Fig. S6 The density profile of each component for (a) BSB-Cz/CBP at 450 K, (b) CBP/BSB-Cz at 450 K, and (c) BSB-Cz/CBP at 400 K. The horizontal dashed line indicates 0.9 times of bulk density and vertical dashed lines indicate the intersections (interface boundaries).

Table S2 The interface thickness (Å) evaluated with plane-average method and our method. The relative errors are indicated inside the parentheses.

		CBP/BSB-Cz	BSB-Cz/CBP	CBP/α-NPD	α-NPD/CBP
400 K	Plane-average (relative difference)	11.7 (+40%)	12.6 (+35%)	10.3 (-1%)	10.9 (+2%)
	Our method	8.38	9.33	10.38	10.67
450 K	Plane-average (relative difference)	12.3 (+5%)	16.2 (+47%)	13.2 (+8%)	14.1 (+10%)
	Our method	11.72	11.02	12.20	12.86

Random-walk model

In the one-dimensional random-walk model, molecules are assumed to move only along the z-axis (normal to substrate). The z-displacement is calculated as follows: the height of surface and the displacement is initially set to zero. The step size follows the normal distribution of zero mean and standard deviation of 0.5 Å with a restriction. The

displacement cannot be higher than the height of the surface or lower than the height of the surface minus the thickness of mobile layer. After each step, the height of the surface increases by certain value, which is related to the diffusion coefficient and the deposition rate. If the displacement is lower than the height of the surface minus the thickness of mobile layer, it is considered that the molecule has become immobile and the process is terminated. There are two parameters in the random-walk model; the one is the thickness of mobile layer and the other one is the speed of surface rising, which is related to the diffusion coefficient and deposition rate. Thus, it can be inferred that the degree of intermixing depends on the temperature, surface diffusivity, and deposition rate. The parameter related to the thickness of mobile layer was directly inferred from the deposition simulation of pure CBP film, and the value is 17 Å. The other parameter related to the speed of surface rising is fitted to reproduce z-displacement of deposition simulation and the value was 0.07 Å per step. Fig. S7a illustrates the random-walk process. From the distribution of z-displacement, we can predict the density profile along z-axis. Fig. S7b shows the ideal density profile from random-walk model where A and B are identical.

In this random walk model, the mobility of molecules suddenly becomes zero at the cutoff distance (the boundary between mobile layer and immobile layer). We have compared a random walk model with hard cutoff (the one used in this study) and with soft cutoff (where molecules' mobility decreases linearly and becomes zero at the cutoff distance continuously). Fig. S8 compares the probability distribution of z-displacement for two models. Although the peak position shifted slightly to the left, the overall shape is similar between two models. The result indicates that the use of hard cutoff does not influence the results significantly.
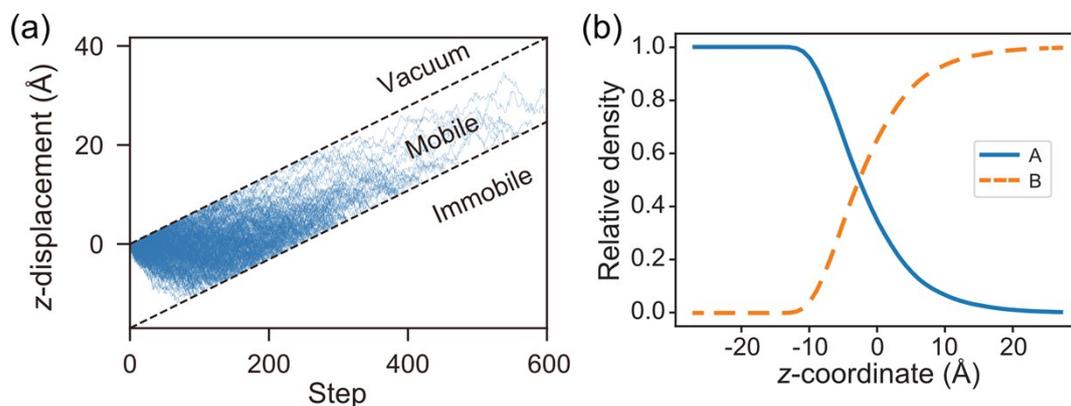
Fig. S7 (a) *z*-displacement vs. random-walk step. Two dashed lines are free surface (up) and the boundary between mobile and immobile layers (down). The position of the free surface and the immobile/mobile boundary shift upward as the process goes on, which corresponds to the growth of the film. The process is terminated when *z*-displacement becomes lower than immobile/mobile boundary. (b) Ideal density profile along *z*-axis obtained from the random-walk model where A and B are identical.
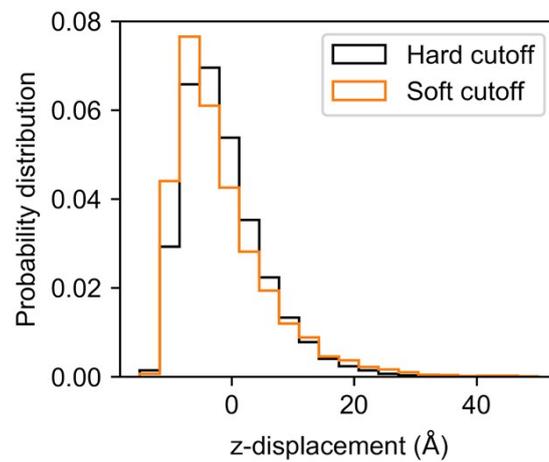

Fig. S8 The comparison of z-displacements in the random-walk model with hard and soft cutoffs.