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All-atom molecular dynamics simulations of vapor deposition as a tool to study thermodynamic stability and structure of organic glasses ✓

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ABSTRACT

Thin films of organic semiconductors obtained by vapor deposition under certain conditions are known to have unique thermodynamic and structural properties, for which they have been named ultrastable. The use of all-atom molecular dynamics simulations for their study is gaining interest due to the possibility of simplifying the process of their deposition and examining their properties at the molecular level. This work provides a systematic and thorough investigation of the key parameters of thin films that characterize their stability and morphology: energy, density, fictive temperature, and orientational order parameter. The results of studying these properties using molecular dynamics for vapor-deposited thin films of three organic semiconductors (TNB, TPB, and TPD) led to a number of valuable insights. First, it was shown that the dependencies of thermodynamic properties on deposition temperature (T_{dep}) obtained from simulations are consistent with those observed experimentally but shifted toward higher temperatures. Moreover, it was demonstrated for the first time that all glass stability indicators for each of the compounds studied show a maximum at a single deposition temperature. These observations highlight the close relationship between T_{dep} and the characteristics of the resulting thin films, which can be used to develop a methodology for producing ultrastable glasses with tunable characteristics. The results of this work show that further application of the molecular dynamics method to study vapor-deposited thin films of organic semiconductors may reveal intriguing aspects of their formation and structure.

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I. INTRODUCTION

Amorphous thin films of organic semiconductors form the basis of many optoelectronic devices, such as OLED displays in TVs, computer monitors, and smartphones. Particular interest lies in the study of thin films obtained by deposition from the vapor phase onto a cold substrate. Under certain conditions of production, they demonstrate unusually high stability,^{1–6} as well as several other unique thermodynamic,^{7–10} mechanical,^{11,12} and optical^{13–15} characteristics. Glasses exhibiting these properties have been termed “ultrastable.” Since their discovery, numerous studies have been conducted to establish the optimal conditions for the production of the most stable glasses and to characterize their properties.^{16–18}

Experimental studies of thin films, however, are highly labor-intensive. This applies to both thermodynamic and, in particular, structural parameters, whose determination requires specialized techniques such as spectroscopic ellipsometry and Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS).¹⁹ Meanwhile, a deep understanding of the thermodynamics and structure of thin films is a key to tailoring their operational properties, particularly the electro-optical features of organic semiconductors.

The limitations of experimental techniques encourage the use of computational approaches to study the properties of vapor-deposited thin films. The most popular choice for this purpose is the method of molecular dynamics (MD). Pioneering work in this area was carried out by Singh *et al.*,²⁰ who simulated the deposition of Lennard-Jones model particles and investigated their

thermodynamic and structural properties. They were the first to show that the difference in stability between vapor-deposited and melt-quenched glasses can be observed using molecular dynamics methods. The majority of studies on vapor deposition simulations focus on the research of thin films of inorganic substances, such as metals^{21–24} and their oxides.^{25,26}

Meanwhile, to date, only a limited number of studies aimed at modeling the deposition of organic semiconductors have been conducted. Lyubimov *et al.*²⁷ performed coarse-grained simulations of the vapor deposition of 4,4'-bis-(*m*-tolylphenylamino)biphenyl (TPD) and determined the energetic and structural parameters of the thin film obtained at a single deposition temperature. In the work of Youn *et al.*,²⁸ the densities and energies of several organic glass-formers were studied based on the results of all-atom simulations, but a complete analysis of these parameters was performed only for one compound—4,4'-bis-(*N*-carbazolyl)-1,1'-biphenyl (CBP). Still, the calculated dependencies of the film properties on deposition temperature deviated from what can be expected from an experiment. For example, the films obtained by MD at temperatures above T_g were characterized by anisotropic molecular orientation, whereas at such temperatures, glasses should exist in an isotropic liquid state. In addition, calculations of the fictive temperature (T_f), one of the key characteristics reflecting the stability of glass, were limited to Ref. 27 only, where it was determined for a single compound at a single deposition temperature. Other examples of the application of molecular dynamics include the study of the deposition of polymer glasses composed of Lennard-Jones particles,²⁹ the structural parameters of thin films of certain organic^{30,31} and organometallic³² semiconductors, and the effect of external electric fields during the vapor deposition process on molecular orientation in the resulting film.³³

MD simulations can become an efficient way to predict the properties of vapor-deposited organic thin films, considering both the molecular structure and deposition regime variations. Furthermore, it may pave the way for developing the pathways for the deposition of the most stable glasses. The necessary step for its implementation is the systematic investigation of the consistency between the modeled and experimental parameters of organic glasses. Nevertheless, no such step has been taken before in all-atom simulations. Actually, much experimental data have been collected on the thermodynamic and structural characteristics of vapor-deposited glasses, depending on the deposition conditions.^{16–18} Even though timescales for the real and MD-simulated processes are different, the current understanding of the regularities observed experimentally enables an adequate comparative analysis.

In this work, we simulate thin film deposition of three typical organic semiconductors [1,3,5-tris-(α -naphthyl)benzene, *N,N,N',N'*-tetraphenylbenzidine, and 4,4'-bis-(*m*-tolylphenylamino)biphenyl] using molecular dynamics and analyze three key parameters that characterize their stability and morphology: energy, density, fictive temperature, and orientational order parameter.

Based on the results obtained, we draw conclusions about the influence of deposition conditions on the thermodynamic and structural characteristics of thin films and obtain a number of intriguing insights into the phenomenon of ultrastable glass formation.

II. COMPUTATIONAL METHODS

In this work, three organic semiconductors were investigated: 1,3,5-tris-(α -naphthyl)benzene (TNB), *N,N,N',N'*-tetraphenylbenzidine (TPB), and 4,4'-bis-(*m*-tolylphenylamino)biphenyl (TPD). The molecules were deposited onto a silicon nitride (Si_3N_4) substrate. All the simulations were conducted with the GROMACS computational package.³⁴

A. Construction of the simulation system

The molecular structures of TNB, TPB, and TPD were taken from quantum-chemical computations made in our previous studies.^{35–37} The topologies of the compounds under study for the GROMOS 54A7 force field³⁸ were created using Automated force field Topology Builder (ATB).³⁹

The structure of the silicon nitride substrate was constructed with the InorganicBuilder plugin implemented in the Visual Molecular Dynamics (VMD) program.⁴⁰ The substrate contained three layers of Si_3N_4 , each of which was a rectangle of 8×8 unit cells with an area of 6.1×6.1 nm. This is more than three times the molecular length of TPD (1.7 nm), which makes the substrate suitable for proper modeling of all three systems. Interaction parameters for silicon nitride were taken from the work of Wendel *et al.*⁴¹

B. Simulation of thin film vapor deposition

Modeling of the vapor deposition of TNB, TPB, and TPD was conducted in the NVT ensemble using the PyThinFilm Python package.⁴² The leapfrog algorithm with a time step of 2 fs was used for the integration of the simulation trajectories. Periodic boundary conditions (PBCs) were implemented in the x and y directions, i.e., in the plane of the substrate. Bonds with hydrogen atoms were constrained using the LINCS algorithm.⁴³ A 1.4 nm cutoff with long-range dispersion correction was used for van der Waals interactions; the same cutoff distance of 1.4 nm was used for Coulomb interactions calculated with the reaction field method.⁴⁴ Temperature coupling was performed using the “v-rescale” thermostat⁴⁵ with a time constant of 0.1 ps.

This work, similar to Refs. 28 and 31, employs a single NVT ensemble for the entire system. In this case, the velocity of the injected molecules decreases gradually until they reach the substrate surface. It is worth noting that there is also another approach, in which newly injected molecules and the substrate are integrated into two independent ensembles: NVE and NVT, respectively. This procedure ensures that the velocity of the injected molecule remains constant throughout its path to the substrate surface, and it slows down only after reaching the substrate surface or film.

Both of these approaches have their own advantages. The choice of the first approach in this study was based on several reasons: (1) The PyThinFilm software package, used to perform the deposition simulations in this study, implements the approach with a single NVT ensemble. (2) The value of the deposition velocity was chosen not to achieve any specific conditions during the simulation but to ensure its successful completion. Therefore, it is not strictly necessary for the molecule's velocity to match the initial value throughout its entire path to the substrate surface. (3) Due to the

relatively high initial speed, low deposition height, and short flight time (10–12 ps), the inclusion of deposited molecules in the thermostat has a small effect on their speed: when approaching the surface of the film, it is only 10%–15% lower than the initial one. Moreover, the slowdown only occurs when the molecule begins to approach the surface of the substrate, as in the experiments, so we believe that describing the deposited molecules using an NVT ensemble is physically justified.

Each deposition cycle consisted of the sequential addition of one molecule of the compound to a simulation cell containing a silicon nitride substrate, with a period of τ_{dep} , during which the energy in the system was equilibrated. The molecules were added at a distance of 5 nm from the upper boundary of the already deposited film. Initial x and y velocity components of each atom within the inserted molecule were sampled from a Gaussian distribution with a mean of 0.0 nm ps⁻¹ and a standard deviation appropriate for the corresponding deposition temperature. The velocities in the z direction were sampled from an analogous distribution but with a mean of 0.5 nm ps⁻¹. This procedure resulted in each deposited molecule acquiring a random non-zero rotational velocity. The initial orientations of the deposited molecules were sampled from a spherical uniform distribution.

In each vapor-phase deposition simulation, the final number of molecules equaled 500. This value corresponds to a film thickness of 11–13 nm. The deposition period (τ_{dep}), i.e., the time between two consecutive additions of molecules to the system, was

500 ps. Thus, the deposition rate (R_{dep}) in the simulations was about $4\text{--}5 \times 10^7 \text{ nm s}^{-1}$, which is a typical value for molecular-dynamics simulations.²⁸ Thin films of each compound were obtained at deposition temperatures (T_{dep}) ranging from 300 K to 500 K in 25 K increments.

The snapshots of vapor-deposited thin films of TNB, TPB, and TPD obtained in this work are shown in Fig. 1.

C. Temperature scanning of obtained glasses

For the investigation of the thermodynamic properties of the deposited films, temperature scans of each system were performed. They consisted of cooling the simulation cell (deposited film on the silicon nitride substrate) from the deposition temperature to 300 K, annealing it at 300 K for 2 ns, and heating the system to 700 K with a scanning rate of 0.05 K ps⁻¹.

Annealing at 300 K and a temperature scan over the range of 300–700 K were also conducted for the empty silicon nitride substrate to be used in further simulation results processing.

For each compound, a sample of melt-quenched glass was also obtained by the following procedure: a thin film deposited at 500 K was heated to 700 K at 0.05 K ps⁻¹, annealed at 700 K for 10 ns, and then cooled to 300 K with the same scanning rate. After that, the annealing and heating procedures mentioned above were conducted. This procedure allowed us to compare the properties of

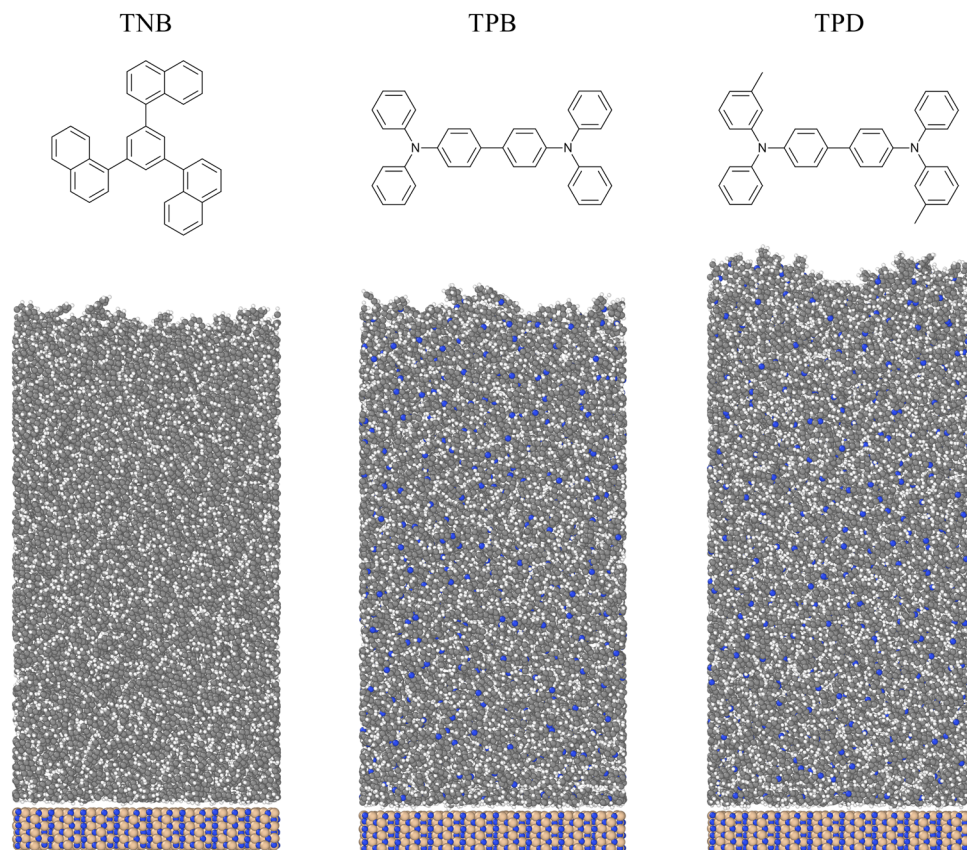


FIG. 1. Thin films of TNB, TPB, and TPD deposited in this work using molecular dynamics at 375, 400, and 400 K, respectively. Atoms of different elements are represented by different colors: gray for carbon, white for hydrogen, blue for nitrogen, and tan for silicon. The snapshots are made with Ovito.⁴⁶

vapor-deposited and melt-quenched glasses under the same conditions. The described algorithm also replicates the experimental method for producing melt-quenched glass as a thin film on a substrate surface, which was employed in one of our previous studies.⁴⁷ The thermodynamic properties of the glass obtained by this method were consistent with those of the bulk melt-quenched sample.

To determine the reproducibility of the simulations, temperature scans for some systems were repeated. The differences in the resulting energies and densities at 300 K did not exceed 0.2 kJ mol⁻¹ and 2 kg m⁻³, respectively.

D. Simulation results processing

The results of the vapor deposition and temperature scanning were used to derive the thermodynamic and structural properties of the obtained glasses: energy (E), density (ρ), fictive temperature (T_f), and orientation order parameter (S).

Another property that is often being mentioned when discussing the stability of thin films is the glass transition temperature (T_g). It is usually determined as the onset of the glass transition peak of the heat capacity temperature dependence. However, obtaining precise thermodynamic quantities from the derivative of the total energy of the simulated system is a non-trivial task. Moreover, unlike other properties that are being discussed in this paper, the glass transition onset is not a thermodynamic but a kinetic parameter. This means that it is largely dependent on the scanning rate, which is many magnitudes higher in the molecular-dynamics simulation than in the experiment. Therefore, in this work, the glass transition temperatures of melt-quenched and vapor-deposited systems are not discussed.

It is worth noting that no signs of crystallization were observed in any of the simulations due to the short simulation timescale (<1 μ s).

To compare the densities and orientational order parameters of the studied glasses, the “bulk phase region” was defined. To this end, the density profiles of the obtained films along the z -axis (normal to the substrate plane) were examined, and such layers were found in which the density remains constant throughout their entire height. That way, the interfacial and surface regions of the films, which have different densities and orientational order parameters than the bulk phase, will not influence the calculation of these properties. In each case, the thickness of the bulk region was at least 7 nm; it usually ranged between (3–4) and (10–11) nm along the z -axis. The thickness of the interfacial region (closest to the substrate) was 3–4 nm, and that of the surface region was 1–2 nm.

The procedures for calculating the parameters of the deposited films obtained in this work are described below. In the case of energy and density, the comparison was made both under uniform conditions—at 300 K—and across the temperature range of 300–700 K. For the comparison of the film properties at 300 K, the total energies, molar volumes, and orientational order parameters were calculated from the average values during the second half of the annealing step (from 1 to 2 ns). The adjacent-averaging method was used to process the results of temperature scans.

1. Total energy (E)

For each vapor-deposited and melt-quenched glass, the total energy of the simulation cell was calculated using the built-in

GROMACS tool. The energy of the empty silicon nitride substrate was subtracted from the total value to obtain the energy of the organic glass film itself.

2. Density (ρ)

For the calculation of the density of vapor-deposited and melt-quenched glasses, the following procedure was used: the overall mass of all the atoms in the bulk region of the film was found, and then, this value was divided by the volume of the bulk layer. Such a treatment ensures that the areas of the film located close to its surface and, therefore, having a lower density are not taken into account in the calculations. From these densities, the molar volumes of the obtained glasses were derived for further analysis of fictive temperatures.

3. Fictive temperature (T_f)

The fictive temperature of a glass can be determined using three approaches: from the intersection of the (1) energies or (2) molar volumes of the liquid and the glass, or (3) from the comparison of the heat capacity integrals on temperature scans. The latter method requires precise data on the heat capacities of both liquid and glass phases, as it involves their extrapolation onto the common temperature range. The isochoric heat capacities can be obtained from the molecular dynamics simulations in the NVT ensemble by differentiating the total energy by temperature. However, the heat capacity values obtained in this way often contain noise associated with the non-zero response time of the thermostat, and their extrapolation is possible in many ways, leading to completely different results. Energy and molar volume are much less sensitive to fluctuations during simulation; therefore, in this work, the first two methods were used to determine the fictive temperatures.

For this procedure, the energies and molar volumes of melt-quenched glass were used, as the scan of this system covers the widest range of liquid phase existence, which allows achieving the best-fit quality. The fictive temperature was determined by approximating the energy or molar volume of the liquid phase with a quadratic polynomial, extrapolating the obtained dependence to lower temperatures, and finding the intersection point with the corresponding property of the deposited glass. A quadratic polynomial was chosen for the approximation because integrating the heat capacities, which are most often expressed as linear functions of temperature,⁴⁸ yields a quadratic dependence on temperature. The dependence of the molar volumes of liquids and glasses on temperature is more complex, but is also frequently described by quadratic polynomials.^{49–51}

4. Orientation order parameter (S)

The orientation order parameter is widely used in the literature to describe the structural characteristics of glasses, including those deposited by molecular dynamics. It is determined from data on the position of molecules relative to the substrate plane according to the following equation:

$$S = \frac{3\langle \cos^2 \theta \rangle - 1}{2}, \quad (1)$$

where θ is the angle between the normal to the substrate plane and the “molecular vector” and $\langle \cos^2 \theta \rangle$ is the average value of the cosine

of the angle θ for all molecules in the deposited film. In the case of TNB, the normal to the plane of the central benzene fragment was chosen as the “molecular vector”; in the case of TPB and TPD, it was determined as the vector between the nitrogen atoms.

In Sec. III, the characteristics mentioned above will be used to prove that the same patterns are observed for MD-simulated thin films as those obtained from experimental measurements. In addition, the temperatures at which the most stable glasses are deposited will be determined.

III. RESULTS AND DISCUSSION

A. Energy of the simulation cell

A straightforward characteristic indicating the stability of glass is the total energy of the simulated system. It consists of potential and kinetic parts. Potential energy is determined by inter- and intramolecular forces between the atoms of the deposited film, which depend on the distances and angles between them. The most relaxed glasses have molecules arranged in such a way that the deviation of structural parameters from equilibrium values is minimal. Kinetic energy is defined by the velocities of atoms, i.e., the temperature of the system. Since the properties of all thin films are compared at the same temperature of 300 K, they all have the same kinetic energy. Thus, differences in the total energies of the systems are determined by the efficiency of molecular packing in their structures.

The total energies of the deposited thin films of TNB, TPB, and TPD cooled to 300 K are compared to those of the melt-quenched glasses in Table I and Fig. 2.

The same influence of the deposition temperature (T_{dep}) on the energy of the film is observed for all three compounds. The dependence between the film energy and T_{dep} is parabolic, with minima at temperatures of 375 K for TNB and 400 K for TPB and TPD. Hereinafter, these temperatures, at which the most stable films are deposited, will be referred to as T_{ug} . The T_{ug} values are greater than T_g observed at the conventional scanning rates ($\sim 0.1 \text{ K s}^{-1}$). However, one should keep in mind that the deposition rates are also orders of magnitude greater than in typical experimental setups.

The differences in energies between melt-quenched glasses and vapor-deposited ones at T_{ug} for the three compounds studied are in the range of 6–8 kJ mol^{-1} . With a further increase in T_{dep} , the energy of the resulting thin film increases almost linearly and at 500 K reaches a value close to that of the melt-quenched glass. The exception is TPD, for which the deposition temperature at which completely isotropic glass is formed exceeds 500 K, which will be confirmed further when examining the orientation order parameter.

The total energy of the system in molecular dynamics simulations can be correlated with the experimental quantity—the enthalpy of glass. The determination of the difference between the enthalpies of melt-quenched and vapor-deposited glass is possible using the temperature dependencies of the heat capacities of liquid and glass. However, this procedure is often complicated by the crystallization of the sample just above T_g and the high sensitivity of the calculation results to uncertainties in the heat capacity measurements. Recently, we have proposed an approach for the direct determination of the glasses' stability using solution calorimetry.⁴⁷ Using this method, the difference in enthalpies between vapor-deposited at $T = 0.85 T_g$ and melt-quenched glasses for TNB was determined to be $-4.2 \pm 0.5 \text{ kJ mol}^{-1}$. According to the results of the present study, the maximum value of ΔE reaches -8.2 kJ mol^{-1} , which is almost twice as much. There is only a qualitative, but not quantitative, agreement between these values. The deviation likely comes from differences in the reference states (MQ glasses) used for comparing ΔH or ΔE values in the experiment and in the simulation. They differ significantly because they were obtained at different scanning rates: $1\text{--}10 \text{ K min}^{-1}$ (experiment) vs $5 \times 10^{10} \text{ K s}^{-1}$ (simulation). Thus, the larger value of ΔE obtained in this study may be the result of the higher energy of the melt-quenched glass. For a direct comparison of the system's enthalpy with experimental data, the simulation protocol should be further developed.

The resulting temperature dependence of the total energy of the simulated systems (see Fig. 3) is consistent with that of the experimental enthalpies of glass and liquid, which can be obtained by integrating their heat capacities.^{2,6} Melt-quenched glasses are characterized by a continuous curve with a smooth change in slope at

TABLE I. Energies (E) of thin films of TNB, TPB, and TPD deposited at different temperatures (T_{dep}) and their differences (ΔE) from the energies of the melt-quenched glasses, compared at $T = 300 \text{ K}$. Values corresponding to thin films with the lowest energies are highlighted in bold.

T_{dep} (K)	TNB		TPB		TPD	
	E (kJ mol^{-1})	ΔE (kJ mol^{-1})	E (kJ mol^{-1})	ΔE (kJ mol^{-1})	E (kJ mol^{-1})	ΔE (kJ mol^{-1})
300	249.4	−7.3	179.8	−2.6	118.3	−3.3
325	248.9	−7.9	178.0	−4.4	116.0	−5.5
350	248.6	−8.1	177.7	−4.7	115.6	−6.0
375	248.6	−8.2	176.6	−5.8	114.4	−7.2
400	249.0	−7.8	176.2	−6.3	113.9	−7.7
425	250.3	−6.5	176.2	−6.2	114.1	−7.5
450	252.2	−4.5	177.8	−4.6	114.8	−6.7
475	254.0	−2.8	180.4	−2.0	117.8	−3.8
500	255.9	−0.9	182.3	−0.1	119.6	−2.0
MQ glass	256.8	0.0	182.4	0.0	121.6	0.0

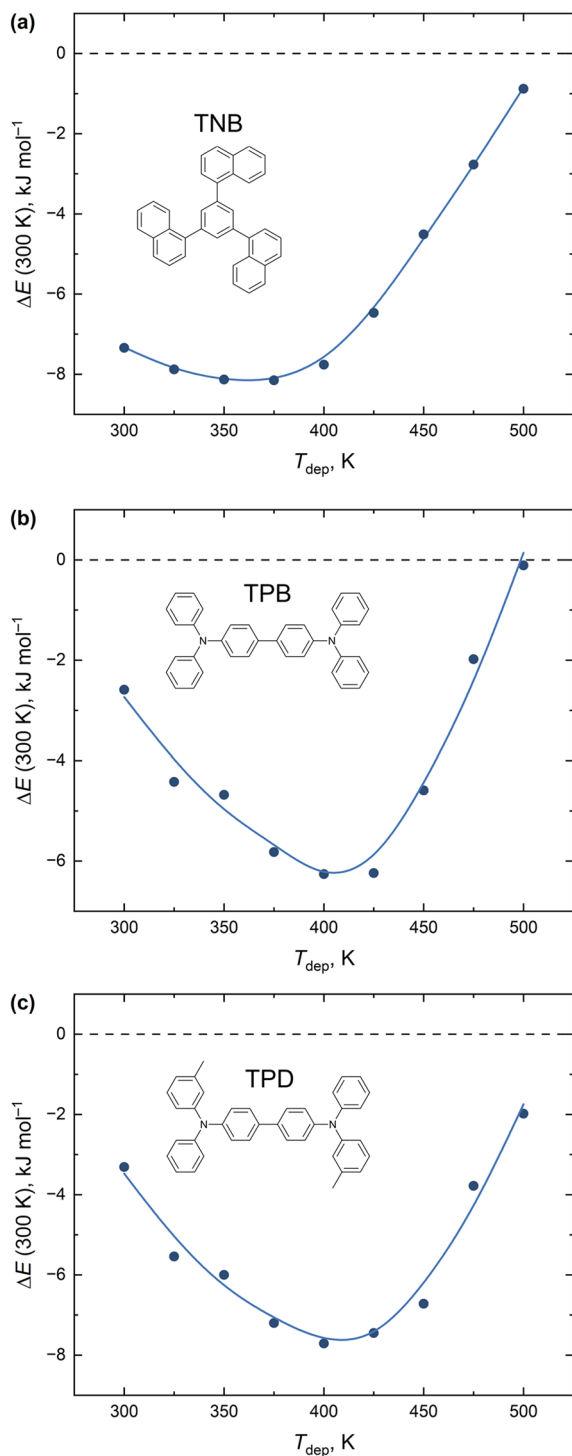


FIG. 2. Differences between the energies of thin films of (a) TNB, (b) TPB, and (c) TPD deposited at different temperatures and those of the melt-quenched glasses, compared at $T = 300\text{ K}$. The curved lines are guides to the eye.

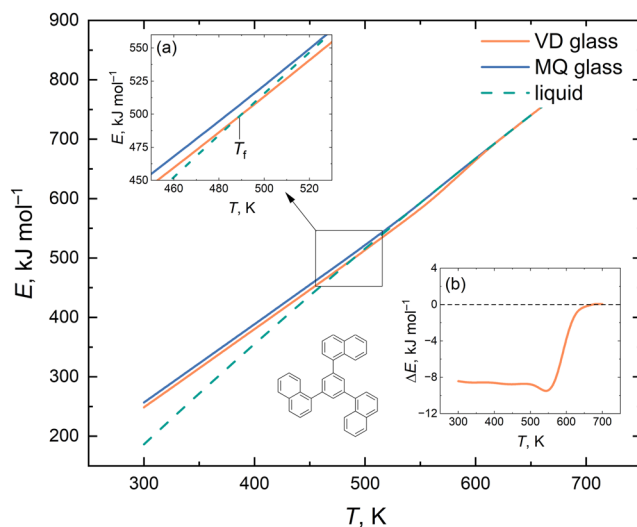


FIG. 3. Temperature dependence of the total energy of vapor-deposited at $T_{\text{dep}} = 375\text{ K}$ (VD glass, orange line) and melt-quenched (MQ glass, blue line) thin films of TNB. The dashed line indicates the extrapolation of the energy of the liquid. Inset (a) highlights the intersection of the liquid and glass energies, which is used to determine the fictive temperature (T_f). Inset (b) demonstrates the change in the difference between the energies of VD and MQ glasses during temperature scanning.

the glass transition temperature. In the case of ultrastable films, the observed curve has a sigmoidal shape with an additional segment corresponding to an abrupt increase in energy to the level of an isotropic liquid. In this regard, the glass transition in ultrastable films resembles a first-order phase transition. This has formed the basis for some hypotheses about the structure of these films, which will be discussed further in Sec. III G.

Figure 3 also shows examples of the extrapolation of the liquid energy to the low-temperature region, which was used to find the fictive temperatures of the obtained films by intersection with the glass energies.

The above-described patterns can be observed more clearly by looking at the temperature dependence of the molar volume of thin films, which exhibits similar trends and will be discussed in Sec. III B.

B. Density and molar volume

It has been repeatedly noted that vapor-deposited thin films have 1%–2% higher densities than the “ordinary” melt-quenched glasses.^{1,9,10,52} Thus, the denser packing of the molecules in the structure of the glass contributes to its greater thermodynamic stability.

As for energies in Sec. III A, the densities of the vapor-deposited films at 300 K were compared to those of the melt-quenched glasses (see Table II and Fig. 4). The density–temperature dependencies show positive peaks at T_{dep} of 375 K for TNB and 400 K for TPB and TPD. Thus, the maxima on the deposition temperature dependence of the film density coincide with the lowest energy thin films for all compounds under study.

TABLE II. Densities (ρ) of thin films of TNB, TPB, and TPD deposited at different temperatures (T_{dep}) and their differences ($\Delta\rho$) from the densities of the melt-quenched glasses, compared at $T = 300$ K. Values corresponding to thin films with the highest densities are highlighted in bold.

T_{dep} (K)	TNB		TPB		TPD	
	ρ (kg m ⁻³)	$\Delta\rho$ (%)	ρ (kg m ⁻³)	$\Delta\rho$ (%)	ρ (kg m ⁻³)	$\Delta\rho$ (%)
300	1148.0	1.6	1124.1	2.0	1094.7	1.5
325	1149.9	1.7	1123.8	2.0	1099.6	1.9
350	1150.1	1.8	1124.9	2.1	1099.9	2.0
375	1151.3	1.9	1127.9	2.3	1103.8	2.3
400	1147.1	1.5	1129.6	2.5	1105.9	2.5
425	1144.2	1.3	1125.0	2.1	1102.7	2.2
450	1138.9	0.8	1120.1	1.6	1094.5	1.5
475	1134.2	0.4	1108.4	0.5	1087.9	0.9
500	1131.6	0.1	1101.7	0.0	1078.4	0.0
MQ glass	1129.9	0.0	1101.5	0.0	1078.2	0.0

The normalized thickness is most often used in the analysis of experimental parameters of thin films, rather than density, since the latter quantity is challenging to measure. Xiang *et al.*⁵³ proposed a method for determining the density of organic thin films using a spectrophotometer and a surface profiler and obtained a density of vapor-deposited TPD equal to 1.08 g cm⁻³. Chen *et al.*^{54,55} also applied this method to measure the density of TPD thin films, which turned out to be 1.10 g cm⁻³. The latter value is in excellent agreement with the densities of the most stable glasses obtained in this work using MD simulations. The first value from the work by Xiang *et al.* is slightly lower, which may indicate that the deposition conditions in Ref. 53 were not optimal for the formation of ultrastable films. Indeed, the description of the experimental procedure in this work did not specify the substrate temperature, and the deposition rate varied widely (0.2–4.0 Å s⁻¹).

It is also important to compare trends in molar volume changes of simulated and experimental systems during temperature scanning of thin films. A typical situation observed in experimental studies is illustrated in Refs. 9, 17, 56, and 57 and qualitatively matches with the temperature dependence of the enthalpy of glass. The curve reflecting the temperature dependence of the normalized thickness of melt-quenched glasses contains two sections corresponding to the amorphous and liquid phases and one inflection point in the transition between them. In the case of ultrastable glasses, both qualitative and quantitative differences are observed: the appearance of an intermediate section of the curve between the molar volumes of glass and liquid and a shift of the glass transition toward higher temperatures. Figure 5 demonstrates that these features are also characteristic for thin films obtained using the molecular dynamics simulations. It also illustrates the second method for finding the fictive temperature based on the intersection of the molar volumes of glass and supercooled liquid.

C. Fictive temperature

One of the main parameters used for the characterization of the glass stability is the fictive temperature (T_f). It corresponds to the point at which the properties of glass coincide with those of

a supercooled liquid. The work of Gao and Simon⁵⁸ demonstrated that, unlike T_g , the fictive temperature is independent of the heating rate used for its determination. This feature makes T_f convenient for analysis with the molecular dynamics method, as it minimizes the effect of very high scanning rates during simulations.

It is known that fictive temperatures obtained experimentally using the energetic and volumetric data differ from each other but have the same tendencies.⁵⁹ To prove that these patterns also hold true for simulated thin films, we calculated fictive temperatures using both methods: based on the intersections of total energies and molar volumes of liquid and glass. The results of T_f determination are presented in Table III and Fig. 6.

Indeed, fictive temperatures determined from data on energies and molar volumes sometimes differ by 5–10 K, but their overall dependence on deposition temperature remains constant. It fits with the trend previously observed for the total energies of the systems: the minimum values of T_f for TNB, TPB, and TPD are observed at T_{dep} of 375, 400, and 400 K, respectively. Thus, thin films deposited at these temperatures are the most stable by all three indicators: energy, density, and fictive temperature.

In many studies devoted to the experimental study of the properties of thin films, a difference of 20–30 K between the fictive temperatures of ordinary and ultrastable glasses has been reported.^{5,17,47,60} A similar situation is observed for the systems obtained in this work using molecular dynamics: the difference between the fictive temperatures of vapor-deposited at T_{ug} and melt-quenched thin films is 39 K on average.

D. Orientation order parameter

The orientation parameter (S) is a structural characteristic that is often considered when discussing the properties of thin films of organic semiconductors. The value of S reflects the predominant orientation of molecules in the system relative to the substrate plane. Depending on the selected “molecular vector,” the orientation parameter data are interpreted in different ways. For TNB, $S = 1$ indicates a parallel arrangement of film molecules relative to the substrate, $S = -0.5$ denotes a perpendicular arrangement, and $S = 0$ indicates an

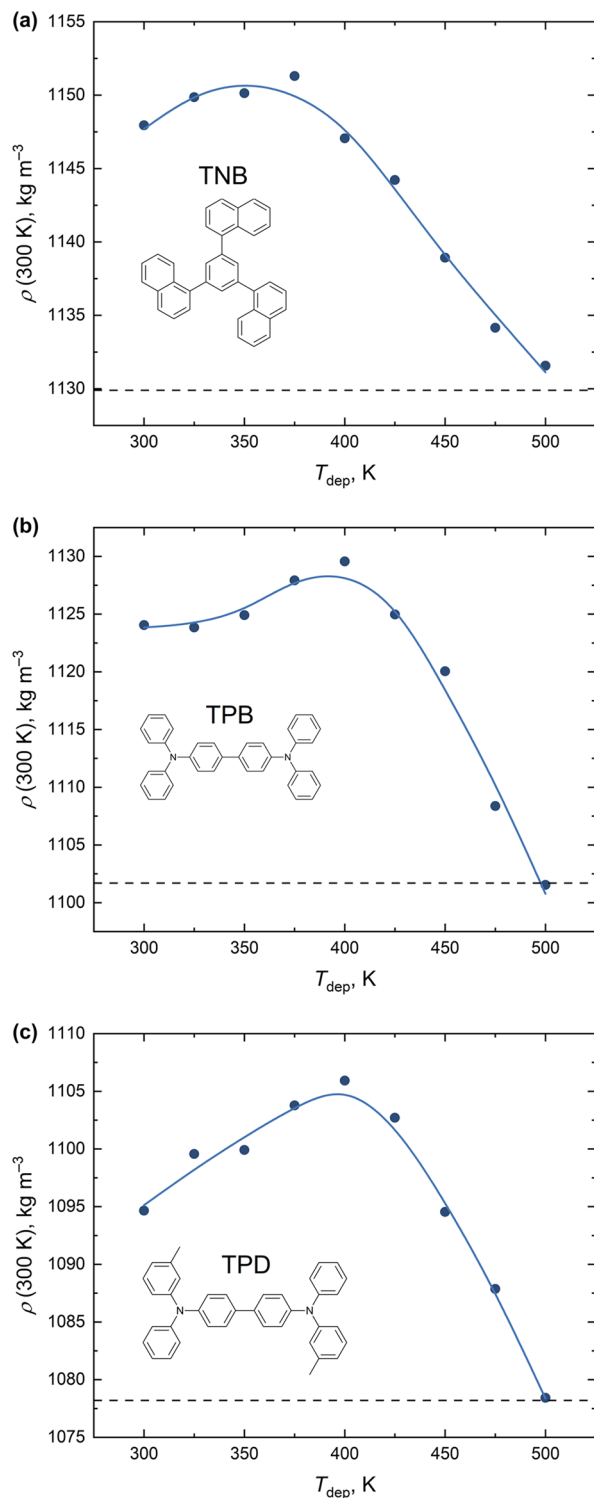


FIG. 4. Densities of thin films of (a) TNB, (b) TPB, and (c) TPD deposited at different temperatures, compared at $T = 300 \text{ K}$. The dashed lines indicate the densities of the melt-quenched glasses. The curved lines are guides to the eye.

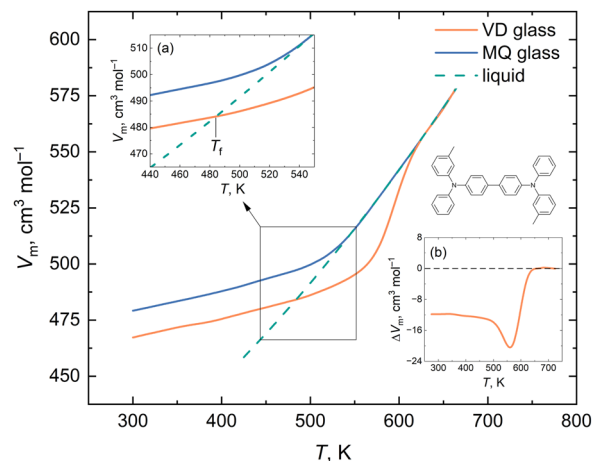


FIG. 5. Temperature dependence of the molar volume of vapor-deposited at $T_{\text{dep}} = 400 \text{ K}$ (VD glass, orange line) and melt-quenched (MQ glass, blue line) thin films of TPD. The dashed line indicates the extrapolation of the molar volume of the liquid. Inset (a) highlights the intersection of the liquid and glass molar volumes, which is used to determine the fictive temperature (T_f). Inset (b) demonstrates the change in the difference between the molar volumes of VD and MQ glasses during temperature scanning.

TABLE III. Fictive temperatures (T_f) determined based on the data on the energies (E) and molar volumes (V_m) of thin films of TNB, TPB, and TPD deposited at different temperatures (T_{dep}). Values corresponding to thin films with the lowest fictive temperatures are highlighted in bold.

T_{dep} (K)	T_f (K)					
	TNB		TPB		TPD	
	E	V_m	E	V_m	E	V_m
300	492	498	501	502	521	515
325	489	493	495	489	509	503
350	488	491	491	487	505	499
375	486	483	483	474	500	495
400	487	487	479	471	496	484
425	491	493	480	477	499	487
450	497	500	488	485	500	496
475	505	507	498	505	511	508
500	514	516	517	524	517	521
MQ glass	518	519	525	525	525	523

isotropic distribution of angles between the molecule vector and the substrate. In the case of TPB and TPD, parallel, perpendicular, and isotropic arrangements correspond to orientation parameter values of -0.5 , 1 , and 0 .

The orientational order parameters of the deposited thin films TNB, TPB, and TPD depending on the deposition temperature are presented in Table IV and Fig. 7.

The dependencies of the thin film orientation parameter on the deposition temperature for TNB, TPB, and TPD qualitatively agree with those observed experimentally for molecules of similar shape;

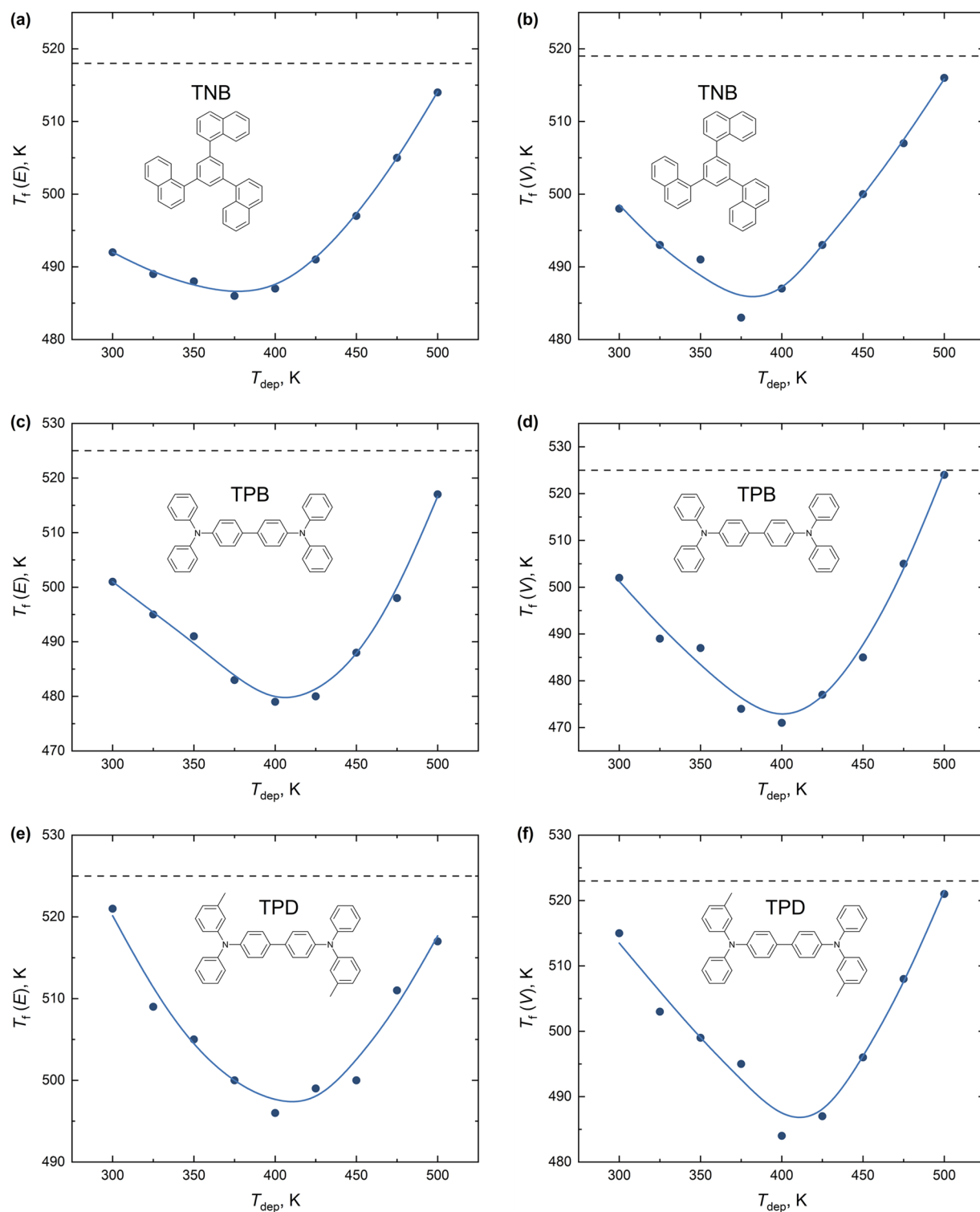


FIG. 6. Fictive temperatures determined based on the data on the energies (left column) and molar volumes (right column) of thin films of [(a) and (b)] TNB, [(c) and (d)] TPB, and [(e) and (f)] TPD deposited at different temperatures. The dashed lines indicate the fictive temperatures of the melt-quenched glasses. The curved lines are guides to the eye.

TABLE IV. Orientational order parameters (S) of thin films of TNB, TPB, and TPD deposited at different temperatures (T_{dep}), compared at $T = 300$ K.

T_{dep} (K)	S		
	TNB	TPB	TPD
300	0.383	-0.261	-0.210
325	0.363	-0.281	-0.244
350	0.325	-0.282	-0.254
375	0.251	-0.288	-0.284
400	0.171	-0.298	-0.235
425	0.090	-0.253	-0.250
450	-0.070	-0.124	-0.171
475	0.003	0.052	-0.052
500	0.002	0.003	0.027

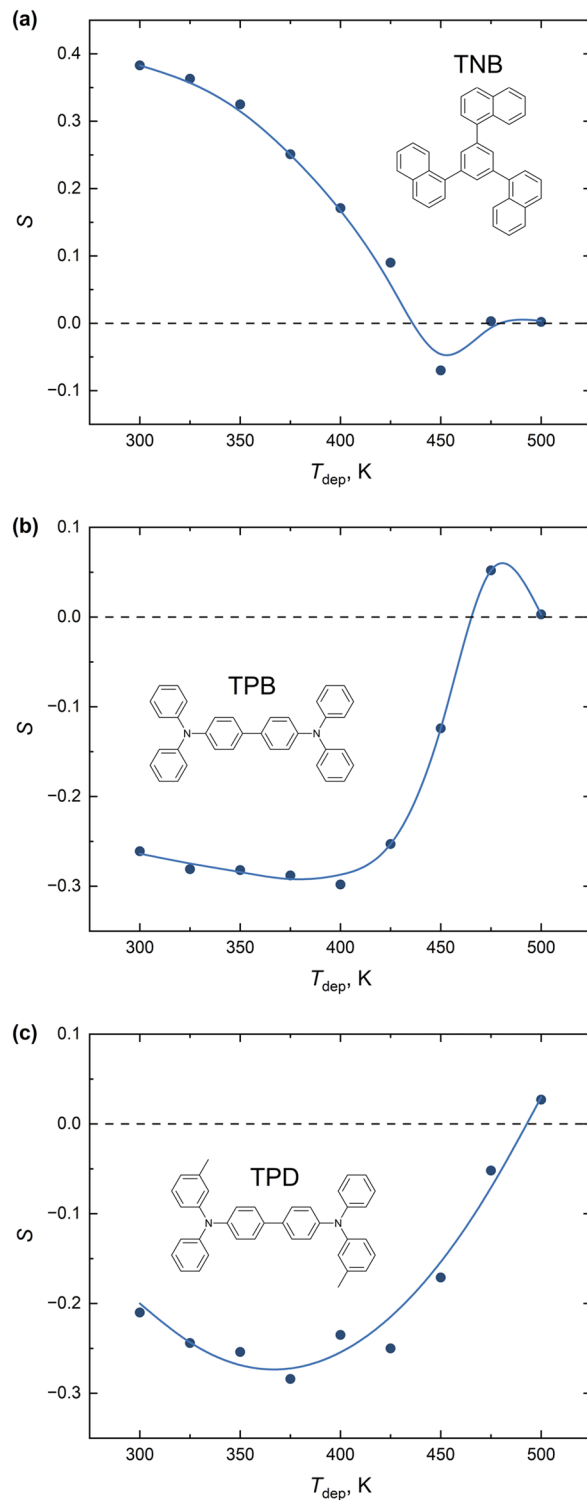
however, as in the case of thermodynamic properties, they are shifted toward higher temperatures.

The orientation parameter of TNB is maximum at the lowest deposition temperatures and decreases monotonically with increasing T_{dep} . In the case of TPB and TPD, the orientation parameter reaches a minimum at a temperature of T_{ug} or slightly lower, which is not typically observed in experiments. There may be several reasons for this. First, the TPD data presented in experimental papers^{1,30} range down to $0.65 T_g$ and do not go below that temperature. It is possible that at lower temperatures, the experimental data might show the same pattern as observed in the simulation. Second, in the experimental determination of the orientation order parameter, the entire film is analyzed, including the interfacial and surface regions, whereas molecular dynamics allows the bulk region to be studied separately. If the majority of molecules in the interfacial and surface regions are oriented parallel to the substrate, they can significantly influence the obtained value of the orientation order parameter.

Similarly, in agreement with the experimental results, all three compounds have a deposition temperature range in which the film has a preferred perpendicular orientation of molecules relative to the substrate plane. Right afterward, the orientation parameter takes on a value close to zero, which indicates the deposition of isotropic glass at higher temperatures. As noted when considering film energies, for TPD, this occurs at $T_{\text{dep}} > 500$ K, and therefore, a limit of $S = 0$ is not observed in Fig. 7(c).

In the work of Yokoyama,¹⁵ it was demonstrated that the predominantly horizontal orientation of molecules on the substrate contributes to the improvement in both the electrical and optical properties of OLEDs. For the most stable TPB and TPD films obtained in this work, fairly low orientation parameter values are also observed. This may indicate that at $T_{\text{dep}} = T_{\text{ug}}$, the deposited thin films exhibit a unique combination of thermodynamic and electro-optical properties.

However, as will be noted in Sec. III E, most modern theories of ultrastable glass formation assume that the planar arrangement of molecules relative to the substrate reduces the thermodynamic stability of the film. This contradiction may lead to the conclusion that the orientational order parameter, despite being a useful characteristic, may not be sufficient for a complete characterization of the

**FIG. 7.** Orientational order parameters of thin films of (a) TNB, (b) TPB, and (c) TPD deposited at different temperatures, compared at $T = 300$ K. The dashed lines indicate the S value for completely isotropic glass. The curved lines are guides to the eye.

morphology of organic semiconductor glasses. It reflects the overall anisotropy of the film but does not provide information about the conformational state of flexible molecules and their deviation from the planar structure. A further detailed study of the distribution of rotating tops' dihedral angles and complex interactions of molecular fragments, such as π - π stacking, is feasible using molecular dynamics methods and may provide useful insights into the structure of thin films.

From the above, it can be concluded that the dependencies of both thermodynamic and structural parameters of vapor-deposited glasses obtained in this work using the molecular dynamics method are in excellent agreement with experimental data. It is important to note that a shift in the characteristics of the glass with respect to the deposition temperature is observed, while the overall pattern remains unchanged. This suggests that high deposition rates will cause the optimal glass deposition temperature (T_{ug}) to shift toward higher temperatures and result in an increase in fictive temperature. Conversely, as the deposition rate decreases, the fictive temperatures will gradually reduce to experimentally observed values. This assumption can be considered from the perspective of the proposed mechanism of ultrastable glass formation.

E. Mechanism of the influence of deposition temperature on the stability of thin films

The observed patterns in changes in glass properties with deposition temperature fully agree with the modern understanding of its influence on the stability of thin films.^{17,18} The main subject in this discussion is the difference in the mobility of molecules on the surface layer, at some distance from the surface (mobile layer), and in the depths of the film. Molecules located in the surface layer are usually oriented parallel to the film plane, while those in the mobile layer can reorient themselves to reach an equilibrium position. Molecules deep within the film remain "trapped" in the positions they occupied after passing through the previous stages.

Glasses obtained at the lowest deposition temperatures exhibit slightly higher energies and lower densities due to a very narrow mobile layer. Therefore, molecules on the film surface that were oriented parallel to the substrate are almost immediately "arrested" in the film bulk and are unable to undergo further equilibration. These considerations are also consistent with the results of determining the orientational order parameter in this work, which in most cases shows the largest fraction of molecules oriented parallel to the film plane at lower temperatures. In addition, the parallel orientation of molecules in the film leads to suboptimal packing, which in turn results in a decrease in its density. However, in the case of TPB, the lowest values of S were observed for the most stable glass, which may indicate that the orientation of molecules in the film and its thermodynamic properties are not always unambiguously related.

Increasing the deposition temperature to T_{ug} while maintaining the deposition rate leads to an increase in the mobility of film molecules and the possibility of their reorientation even in layers located at some distance from the surface. In addition, even after leaving the mobile layer, further relaxation through aging and layering is possible before these molecules finally enter a completely immobile, "frozen" layer. This increases the stability of the films formed and prevents them from falling into an isotropic glass state.

During this process, the film also undergoes densification, which can be observed in Fig. 4.

As the deposition temperature rises above T_{ug} , the height of the mobile layer also increases, allowing the molecules to reach a more complete equilibrium, resulting in the formation of a more isotropic glass. Meanwhile, a gradual decrease in the difference $T_{\text{f}} - T_{\text{dep}}$ is observed. This continues until these values become equal ($T_{\text{f}} = T_{\text{dep}}$) and the deposition of equilibrated liquid begins.

Based on the data obtained in this work (Table III), the difference between T_{f} and T_{dep} decreases from ~ 200 K at $T_{\text{dep}} = 300$ K to 15–20 K at $T_{\text{dep}} = 500$ K. This implies that, in the simulations, the deposition temperature at which T_{f} equals T_{dep} is slightly higher than 500 K for all compounds. These considerations are consistent with the dependencies of the energy, density, and orientation order parameter on the deposition temperature presented earlier in this work.

The shift in T_{ug} observed in the simulation compared to the experiment can be explained as follows. An increase in the deposition rate causes molecules to spend less time in the mobile layer and to have less time for relaxation. Therefore, the optimal deposition temperature (T_{ug}) shifts toward higher temperatures, since molecules must have greater mobility to achieve the same degree of relaxation as at a lower T_{dep} .

This means that the morphology and stability of the deposited glass are determined by the balance between two factors: the deposition rate, which controls the time a molecule spends in a specific layer of the film, and the mobility of the molecules, which is determined by the deposition temperature.^{17,61} Finding the relationship between these characteristics will allow us to predict the temperature at which the most stable glass can be obtained at a given deposition rate.

F. Relationship between deposition rate and substrate temperature at which the most stable glass is formed

In 2007, Ediger's group showed that the most stable indomethacin glasses can be obtained by vapor deposition at $T_{\text{ug}} = 0.85 T_{\text{g}}$.² Since then, many studies have confirmed this observation for a large number of organic compounds.¹⁸ However, it is worth noting that the conditions under which the thin films were produced and studied in these studies varied only slightly: the experiments usually consisted of vapor deposition at R_{dep} of 0.1–1 nm s⁻¹ and determination of T_{g} by heating the substance at a scanning rate of 1–10 K min⁻¹. At the same time, the results of both these procedures depend on the rates at which they are carried out. In this regard, the temperature of 0.85 T_{g} might not be universal but is determined by the conditions of film deposition and analysis.

It is of interest to compare $T_{\text{ug}}/T_{\text{g}}$ for the *in silico*-deposited glasses. In order to evaluate the latter quantity, we used the fictive temperatures of the melt-quenched glasses instead of T_{g} . $T_{\text{f(MQ)}}$ is close to the glass transition temperature (i.e., half-step T_{g}) of a glass if it is prepared at the same cooling and heating rates. Their experimental differences are reported to be within 1.5 K.^{58,62} Based on the calculations provided in the work of Badrinarayanan *et al.*,⁶² we expect that, at the extreme scanning rates, the difference is still within 3 K.

For the three compounds considered in this work, $T_{\text{ug}}/T_{\text{f(MQ)}}$ averaged 0.75. The deviation from the experimentally observed ratio of 0.85 should not be surprising. The deposition rates were $(4\text{--}5) \times 10^7 \text{ nm s}^{-1}$ and the scanning rates were $5 \times 10^{10} \text{ K s}^{-1}$, being by ~ 8 and ~ 11 orders of magnitude greater than in typical experiments. Still, the regularities in the change of thermodynamic properties with deposition temperature were identical to those observed for experimentally obtained films but shifted by 70–100 K. Furthermore, a direct comparison with real systems would at least require keeping the ratio of the deposition and scanning rates the same as the experimental. At the qualitative level, decreasing the cooling and heating rates at which melt-quenched glass is studied should decrease $T_{\text{f(MQ)}}$ and increase $T_{\text{ug}}/T_{\text{f(MQ)}}$.

The relationships between the glass production conditions and their stability have already been discussed in the literature. In recent studies by Prof. Ediger's group,^{63,64} a universal relationship known as Rate-Temperature Superposition (RTS) was established. It connects the deposition rate and substrate temperature via the compound's relaxation time and states that an increase in R_{dep} has the same effect on the properties of the resulting film as a decrease in T_{dep} . Thus, a change in the deposition rate leads to an apparent change in the deposition temperature. Using the RTS approach, one can determine the shift factor—the amount by which the apparent deposition temperature shifts when the deposition rate changes.

The shift in the temperature dependencies of the thermodynamic and structural properties of the glasses, observed in the simulations in this work, is qualitatively consistent with the RTS model. A quantitative comparison requires data from a large number of experimental measurements of the compounds under study, performed at different deposition rates and temperatures. For the compounds mentioned in the work of Bishop *et al.*⁶⁴—itraconazole, posaconazole, and Alq_3 (a common OLED molecule)—the shift factors were 0.18, 0.22, and 0.07 decades K^{-1} . This means that when the deposition rate is increased from 0.1 to $5 \times 10^7 \text{ nm s}^{-1}$, the shift in the temperature dependencies of the thin film parameters for these compounds would be 48, 40, and 124 K, respectively. The last value, obtained for the compound with the structure most similar to those studied in this work, best agrees with the observed shift of 100 K.

Although the results of this study are qualitatively consistent with the RTS approach, when considering the comparison of thin films obtained at very different deposition rates, one must take into account the complications arising from the different timescales themselves and numerous simulation nuances that do not always accurately reflect the experimental deposition protocol.

Overcoming these limitations will allow for an *in silico* evaluation of T_{ug} and the glass stability at different deposition rates. This will facilitate the targeted design of thin films of organic semiconductors by enabling the fine-tuning of the temperature regime of evaporation and deposition. Furthermore, the above considerations call for the continuation of the studies^{13,65,66} devoted to glass vapor deposition at lower rates and particularly lower substrate temperatures. This might be the way to even more stable glasses than were obtained before.

G. Which structural factors define the stability of glass?

Another topic for discussion, on which consensus has yet to be reached, is the structure of ultrastable glasses. Section III E discussed that their unique properties may be the result of aging occurring during the deposition process, but it is not entirely clear what rearrangements occur at the molecular level during this time.

The relative stability of glasses is often attributed to their structural features, particularly to the presence of nanoheterogeneous clusters.^{67,68} It is assumed that “locally favored structures,” characterized by reduced energy and bond orientational ordering, play a crucial role in glass transition and may also be present in ultrastable glasses.⁵¹ This idea is primarily probed via simulations.^{69,70} Danilov *et al.*⁶⁹ performed a computational study, the results of which also led to the conclusion that two phases coexist in stabilized thin films: structured nanoparticles and interfacial regions. A recent study of Leoni *et al.*⁷⁰ also showed a correlation between the stability of vapor-deposited thin films of model glass-formers and the occurrence of locally favored structures.

Meanwhile, Singh *et al.*²⁰ concluded that vapor-deposited glasses made of Lennard-Jones spheres were characterized by more homogeneous packing than melt-quenched ones. They studied structural properties of thin films, such as radial distribution function and average bond-order parameters, which were expected to reveal the presence of heterogeneous local structures. These characteristics turned out to be identical for ordinary and ultrastable glasses. A noticeable difference was observed only when considering the spatial correlations of the order parameters. Particles within ultrastable glasses are less frequently involved in clusters, with a cluster size not exceeding 4 (in the case of ordinary glasses, it can reach 8). Moreover, the coordination environment of particles in ultrastable films was characterized by mainly three types of Voronoi polyhedra, while for ordinary glasses, both a greater number of types and the presence of irregular polyhedra were observed. Thus, the increased stability of vapor-deposited thin films was attributed to a more uniform, homogeneous packing relative to melt-quenched glasses. Some subsequent studies have also linked increased glass stability to the homogenization of local volume fractions⁷¹ or local virial stresses.⁷²

Although the description of the local structure of molecular glasses is more complicated compared to model atomic glasses studied before, we did not observe nanoheterogeneous regions with clear boundaries in the thin films obtained in this work. Nevertheless, they exhibited anisotropy and thermodynamic properties consistent with an experiment. It may necessitate the search for new explanations for their increased stability. The energy of molecular glasses is determined not only by the mutual arrangement of molecules in space but also by their orientation, their valence and dihedral angles, and the possibility of complex intermolecular contacts. Therefore, it is necessary to search for new structural characteristics and parameters that could explain the increased stability of thin films of organic semiconductors. Molecular dynamics can become an indispensable tool for these purposes, as it provides an opportunity to study the individual molecules in the film structure. A more thorough investigation of their local orientation, the mutual arrangement of molecular

fragments, and the dihedral angles between them is the subject of further research, which may clarify the origin of the ultrastability phenomenon.

IV. CONCLUSIONS

In this work, we demonstrate that all-atom molecular dynamics simulations of vapor deposition can be used to obtain ultrastable thin films of organic semiconductors [1,3,5-tris-(α -naphthyl)benzene, N,N,N',N' -tetraphenylbenzidine, and 4,4'-bis-(m -tolylphenylamino)biphenyl], whose thermodynamic properties are consistent with those observed experimentally. A uniform pattern emerges across all considered indicators of glass stability: energy, density, and fictive temperature. All these parameters for each compound have extrema at the same deposition temperature, at which glasses with the lowest energy and the highest density are formed. Changes in the thermodynamic characteristics of thin films during temperature scanning also agree with the dependencies obtained in experimental studies. These findings suggest that all-atom molecular dynamics simulations can be used as a reliable tool for predicting the thermodynamic and sometimes less accessible structural parameters of thin films composed of organic molecules, considering their structure and deposition regime. The development of such protocols will significantly reduce the time and material costs of conducting experimental measurements, as well as expand the possibilities for the research of vapor-deposited thin organic films to the area of ultra-high deposition rates.

Another opportunity offered by the application of molecular dynamics is the possibility to study the structures of the produced glasses in detail at the molecular level. The peculiar properties of the glasses, particularly those of ultrastable ones, are sometimes explained by the presence of nanoheterogeneous domains. In this work, we did not observe cluster-like structures in vapor-deposited organic thin films, at least at the qualitative level of analysis performed. Still, drastic differences in glass behavior, depending on the production conditions, were demonstrated.

Last but not least, the results of this work highlight the close relationship between the deposition rate and the substrate temperature at which the most stable glass is formed. Finding quantitative relationships between these characteristics for compounds of different structures is the cornerstone of developing methods for producing new thin films with unprecedented stability.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Andrey A. Sokolov: Conceptualization (supporting); Formal analysis (lead); Investigation (lead); Methodology (lead); Software (lead);

Visualization (lead); Writing – original draft (lead). **Mikhail I. Yagofarov:** Conceptualization (lead); Formal analysis (supporting); Funding acquisition (lead); Methodology (supporting); Project administration (equal); Supervision (lead); Writing – review & editing (lead).

DATA AVAILABILITY

The data that support the findings of this study are available within the article.

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