Controlling Anisotropy in Vapor-Deposited Glasses

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Introduction

Physical vapor deposition, where the substrate temperature is held within a range close to T_{sub}=0.85T_g, leads to the formation of *stable glasses* [1,2] characterized by

- enhanced thermodynamic and kinetic stability
- high density
- better mechanical properties
- correspond to ordinary glasses aged for a very long time

Recently it has been shown experimentally that vapor deposition of small elongated organic molecules in this range of T_{sub} yields anisotropic molecular orientation, which affects optical properties of glasses.

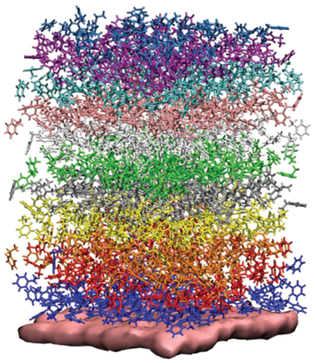
Methods and Models

We perform Molecular Dynamic (MD) simulations that mimic the physical vapor deposition process. The iterative procedure consists of cycles with four stages [3,4]:

- introduce a few new molecules in close proximity of the surface of the old molecules
- equilibrate the newly introduced molecules at higher temperature than the previously deposited.
- linearly cool the new molecules
- energy minimize the entire system

Atomistic simulations of Ethylbenzene were performed using the OPLS all atom forcefield. The model was verified for properties such as density of the liquid.

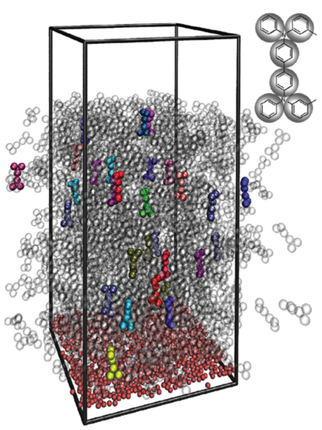
The model captures the experimental T_g of 118K based on the experimental definition. The simulated T_g, however, was found to be 145K. The procedure described above was applied to this model, inserting two molecules each iteration.



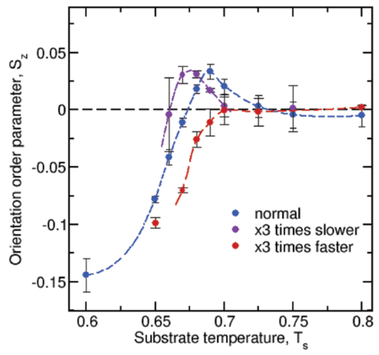
*colored by deposition time

Another systems is a coarse-grained representation of N,N'-Bis(3-methylphenyl)-N,N'-diphenylbenzidine (TPD)

Each TPD molecule consists of six Lennard-Jones spheres connected with stiff harmonic springs and angle potentials.



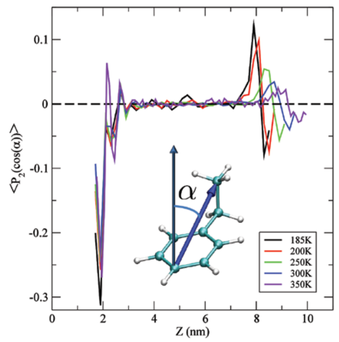
Results

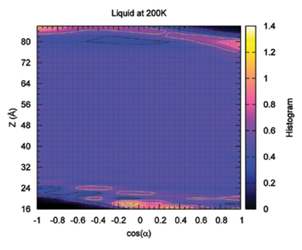


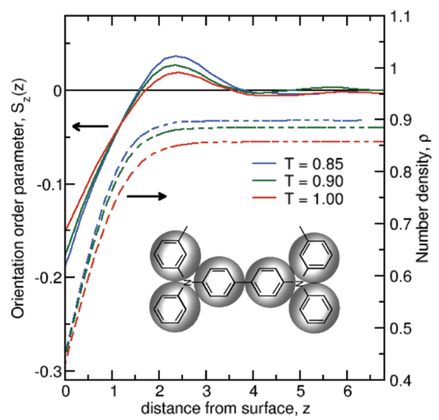
In agreement with experiments the average molecular orientation S_z changes with varying the substrate temperature T_{sub}.

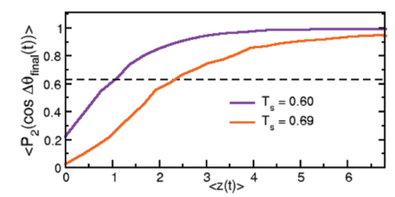
- at $T_{sub}>T_g$ the orientation is random as expected for equilibrium liquid
- for T_{sub} in the range close to 0.85T_g the weak tendency to orient vertically
- at lower T_{sub} the stronger tendency to orient in the plane of the substrate

$$S_z = \frac{3}{2}\langle cos^2\theta\rangle - \frac{1}{2} = \begin{cases} 1, & \text{perpendicular to substrate } (vertical) \\ 0, & \text{random orientation } (isotropic) \\ -\frac{1}{2}, & \text{parallel to substrate } (flat) \end{cases}$$









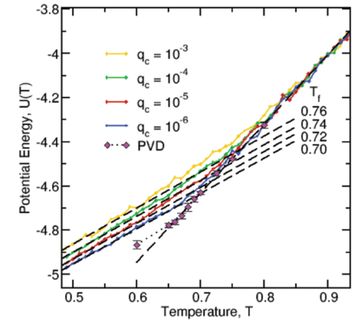
$$\langle P_2(cos\Delta\theta_{final})\rangle = \frac{3}{2}\langle cos^2\Delta\theta_{final}\rangle - \frac{1}{2}$$

The molecular orientation in vapor-deposited glasses can be explained in terms of molecular orientation in the equilibrium liquids near the liquid-vacuum surface (profiles shown above).

In both systems investigated, we see that molecules tend to orient vertically in proximity to the free surface. The effect increases as temperature decreases.

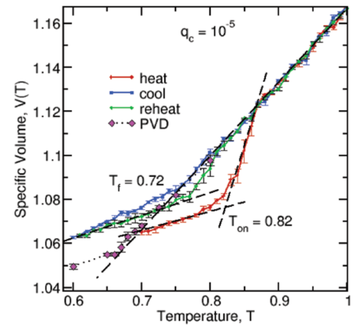
For vapor-deposited films, we calculate the distance from the free surface at which the molecules experience the orientational arrest and correlate it with equilibrium liquid profiles.

Enhanced Thermal Stability



Comparison of the potential energies of ordinary glasses prepared by cooling at various rates with that of the vapor deposited glasses grown with various substrate temperatures.

Fictive temperature dependence on cooling rate is linear and ΔT_f=0.02 per each order of magnitude.



Vapor deposited glasses are 1-2% denser than ordinary glasses.

During heat/cool cycles they show higher melting onset temperature T_{on}, which is a sign of higher kinetic stability over the ordinary glasses.

Conclusion

- In agreement with experiments, it is shown that the degree of anisotropy in vapor deposited glasses can be controlled by tuning the substrate temperature.
- The mechanism of molecular orientation was investigated in atomistic MD simulations of ethylbenzene and MD simulations of coarse-grained TPD molecules.
- The observed dependence on substrate temperature is explained in terms of equilibrium liquid free surface ordering.

Acknowledgements

- Ediger group: Prof. Mark D. Ediger, Shakeel Dalal, Diane Walters (University of Wisconsin-Madison)
- Supported by NSF DMR-1234320
- Computational resources were provided by RCC

References

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