Probing H-bonding Effects on Diffusion in Polymers

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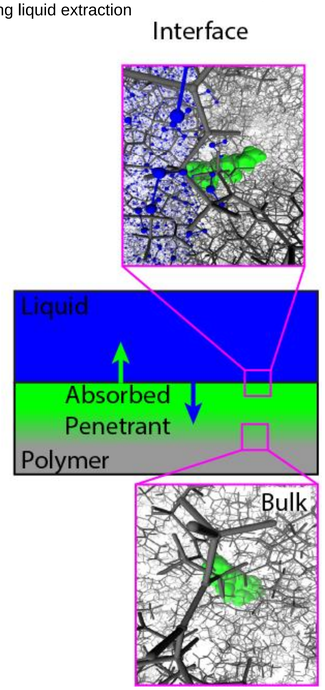
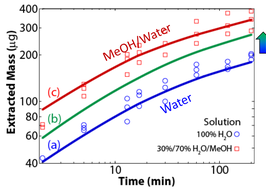
Introduction

Objective: Understand mechanisms responsible for transport enhancement of penetrants absorbed in polymers during liquid extraction



Example: Extraction of VX from silicone elastomer using water and methanol/water mixture



Methanol accelerates VX transport in silicone

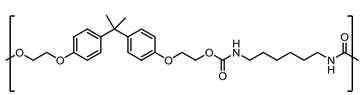
Proposed Mechanisms:

1. Plasticization mechanism (free volume)
2. Mobility disruption mechanism (chain dynamics)
3. Association mechanism (interactions between polymer-solvent-penetrant)

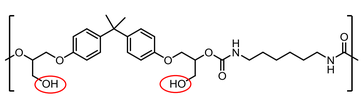
Motivation:

- Polyurethanes are ubiquitous in military coatings
- Scientific interest in reducing penetrant absorption and ability to remove (decon) penetrants in polymers
- To help choose candidate solvents/penetrants
- Searching for diffusion trends across series of increasing H-bond donor/acceptors

Polyurethane (PU)

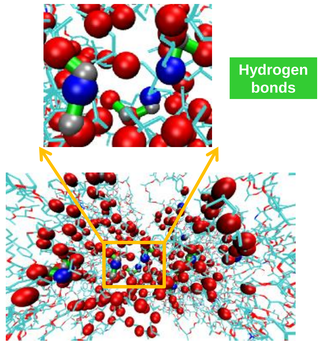


Polyhydroxyurethane (PHU)



Additional H-bond donors

Name	Structure	MW (g/mol)	Molar Volume (cm³/mol)	# H-bond acceptors	# H-bond donors
hexane	H_3C–CH_3	86	127	0	0
Pentylamine	H_3C–NH_2	87	114.7	1	2
BuDiamine	H_2N–NH_2	88	101.9	2	4
pXylene	H_3C–CH_3	106	122.0	0	0
Lutidine	H_3C–CH_3	107	115.2	1	0
DiMePyrazine	CH_3–CH_3	108	108.4	2	0
MeAmine	H_3C–NH_2	31	48.7	1	2
Formaldehyde	$O{=}CH_2$	30	43.8	1	0
MeOH	H_3C–OH	32	40.8	1	1



C.K. Knox, J. Andzelm, et al., 27th Army Sci Conf Proc, Orlando, FL, GP-09 (Dec 2010)

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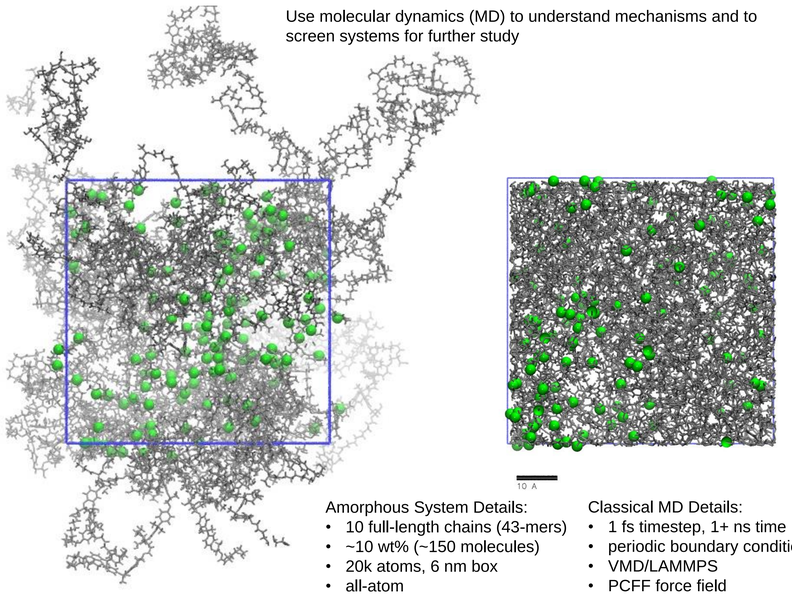
Methods

Use molecular dynamics (MD) to understand mechanisms and to screen systems for further study



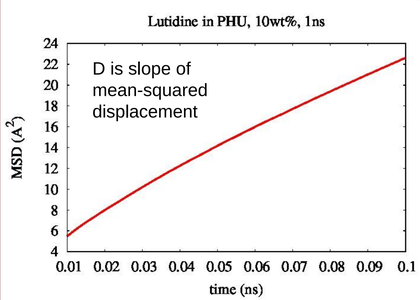
Amorphous System Details:
- 10 full-length chains (43-mers)
- ~10 wt% (~150 molecules)
- 20k atoms, 6 nm box
- all-atom

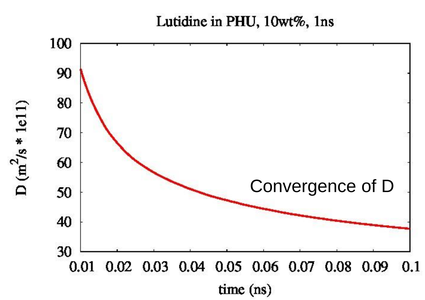
Classical MD Details:
- 1 fs timestep, 1+ ns time
- periodic boundary conditions
- VMD/LAMMPS
- PCFF force field

Approach

- Build PU/PHU polymer systems
- Insert penetrant and solvent molecules with varying H-bonding capacity
- Determine diffusivity and predict IR using MD simulations
- Correlate changes in penetrant mobility (diffusivity) to changing chemical environment due to solvent presence

Diffusivity Calculation





IR Calculation

Fourier transform of total system dipole moment (μ) autocorrelation function (from MD trajectory):

$$I(\omega) = \frac{\hbar\beta}{2\pi}\omega^2 \int dt e^{-i\omega t}\langle \mu(0)\mu(t)\rangle$$

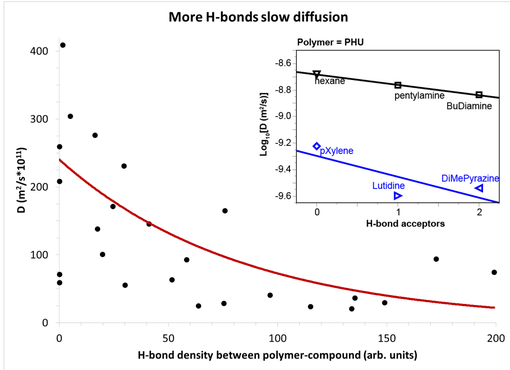
To assign peaks in spectra,
1. select specific atoms (group dipole moment)
2. or turn on/off interactions (e.g., H-bonds) in simulation
3. or perform normal mode (harmonic) analysis

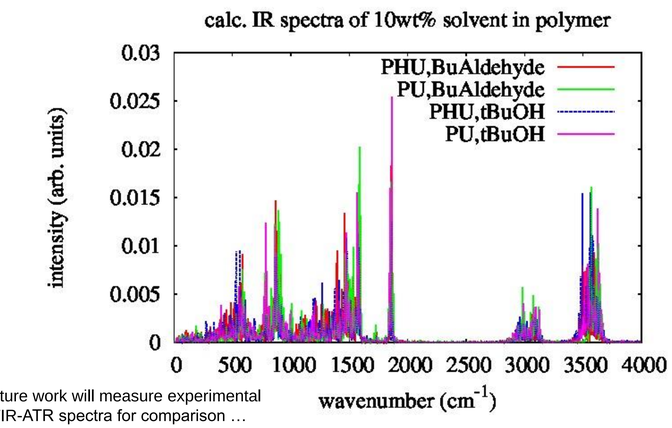
Results

Diffusion Correlations: H-bonds and Sterics

polymer	compound	D ($m^2/s*10^{11}$)	H-bond density
PHU	tBuOH	20.8	133.9
PU	tBuOH	24.3	115.0
PHU	Lutidine	25.3	63.8
PHU	DiMePyrazine	28.8	75.3
PHU	IPA	29.9	148.9
PU	IPA	36.5	135.3
PHU	pyridine	40.9	96.5
PU	pyridine	55.6	30.1
PHU	pXylene	59.5	0.0
PHU	BuAldehyde	63.4	51.6
PU	pXylene	71.6	0.0
PHU	MeOH	74.6	199.1
PHU	Propylaldehyde	93.2	58.3
PU	MeOH	94.1	172.6
PU	BuAldehyde	100.8	19.7
PU	Propylaldehyde	138.6	17.5
PHU	BuDiamine	145.5	41.1
PHU	formaldehyde	165.0	75.8
PHU	pentylamine	171.6	24.6
PHU	hexane	208.4	0.0
PU	formaldehyde	231.1	29.6
PU	hexane	259.4	0.0
PU	pentylamine	276.2	16.3
PHU	TriMeAmine	304.2	5.0
PU	TriMeAmine	409.1	1.5
PHU	DiMeAmine	578.5	23.1
PU	DiMeAmine	906.9	15.9
PHU	MeAmine	1385.6	29.9
PU	MeAmine	1887.2	19.9

* H-bond donor





Future work will measure experimental FTIR-ATR spectra for comparison …

Conclusions

- **Strong H-bonding may slow diffusion** of penetrant molecules thru polymer matrix.
- **Large sizes** of penetrant molecules may also slow diffusion.
- **Aldehyde** diffusion series seemed to vary most between PHU/PU polymers.
- **Methanol** has small size but many H-bonds, resulting in moderate diffusion.

Acknowledgements

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TECHNOLOGY DRIVEN. WARFIGHTER FOCUSED.