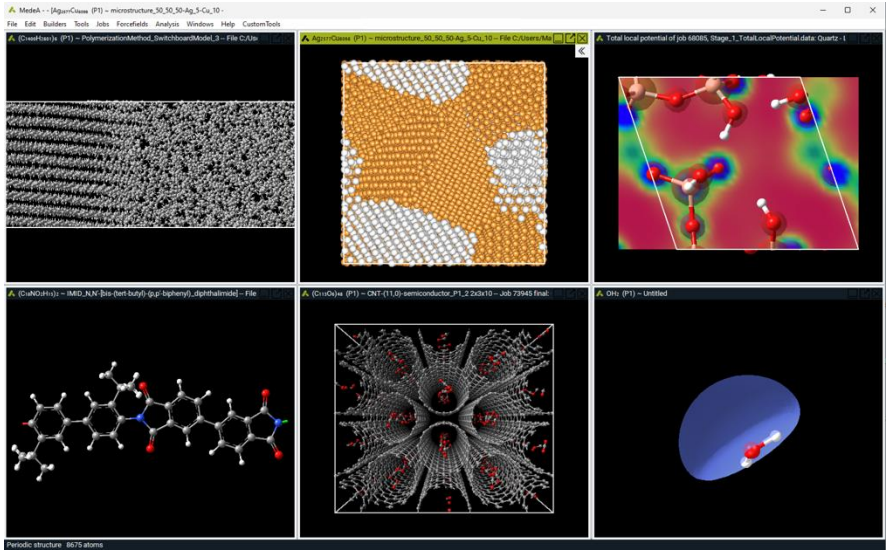
materials design

Introducing the Tailored Design of Polymers



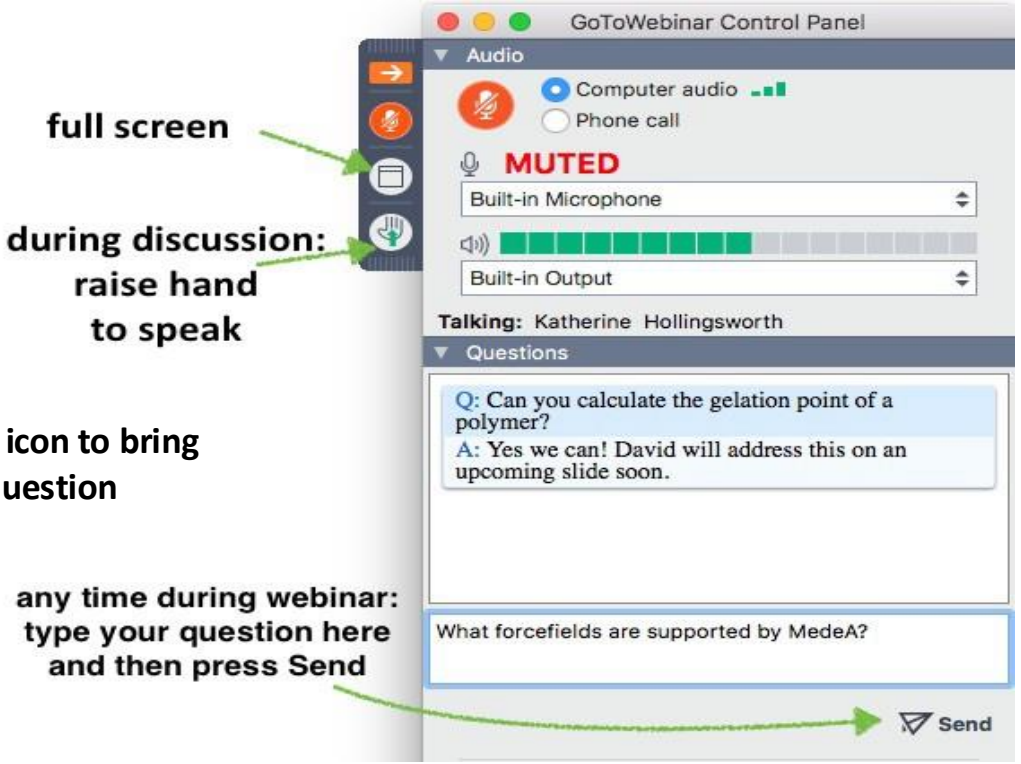
28-30 January 2025

Materials Design Webinar Series

- Each session runs several times to accommodate schedules
  - Share the webinar series with your colleagues!
  - Registration details http://www.materialsdesign.com/webinars
- We will be recording this webinar
  - Watch any of our earlier webinars anytime
  - We will post upcoming webinars on the webinar page
- Vote for the next webinar topic!
  - Take a 2 minutes brief survey at the end of the webinar!
- Audio issues
  - Log out and log back in again
  - Check your audio output
  - Google Chrome (most recent 2 versions) Mozilla Firefox (most recent 2 versions) Apple Safari (most recent 2 versions) Microsoft Edge (most recent 2 versions)

materials design

Please Ask Questions!



Use the raise hand icon to bring attention to your question

any time during webinar: type your question here and then press Send

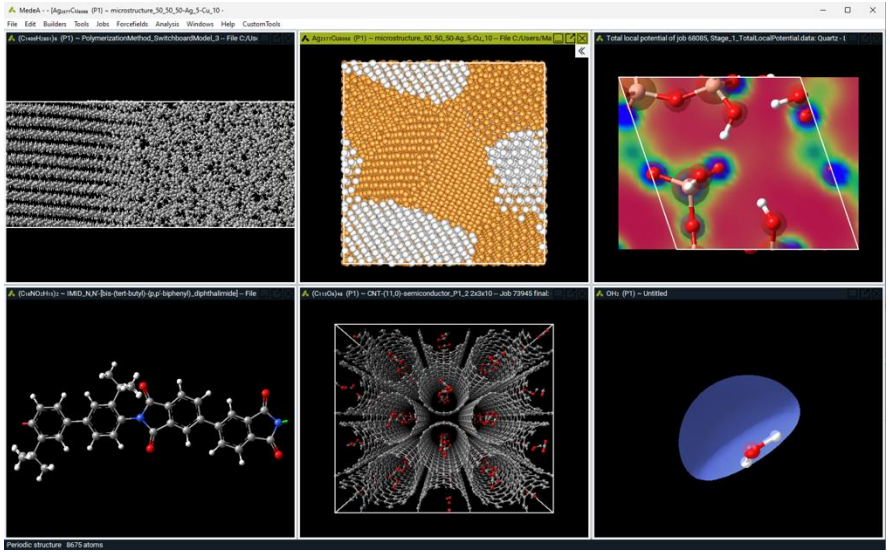
materials design

Webinar Speakers

Katherine Hollingsworth *Dr. Marianna Yiannourakou* *Dr. David Rigby* *Dr. Benoit Minisini*

materials design

Introducing the Tailored Design of Polymers



28-30 January 2025

Databases

Direct access to more than 1,1 million experimental and calculated structure entries

Builders

Rich set of builders for crystalline/amorphous/ordered systems, molecules, interfaces, nanoparticles, polymers, fluids, solids, hybrid materials, composites…

Compute Engines

DFT, classical MD and MC, semiempirical: VASP, GAUSSIAN, MOPAC, LAMMPS, GIBBS

Forcefields + Forcefield Optimizer + MLPG

Access to state-of-the-art Forcefields (non-reactive & reactive); open access to all FF parameters; addition of user-defined FFs; FF optimization, Machine Learning Potential Generator

Workflow Editor and Property Modules

Graphical workflows & pre-configured computational protocols, to facilitate modeling, analysis, and property prediction

High Throughput

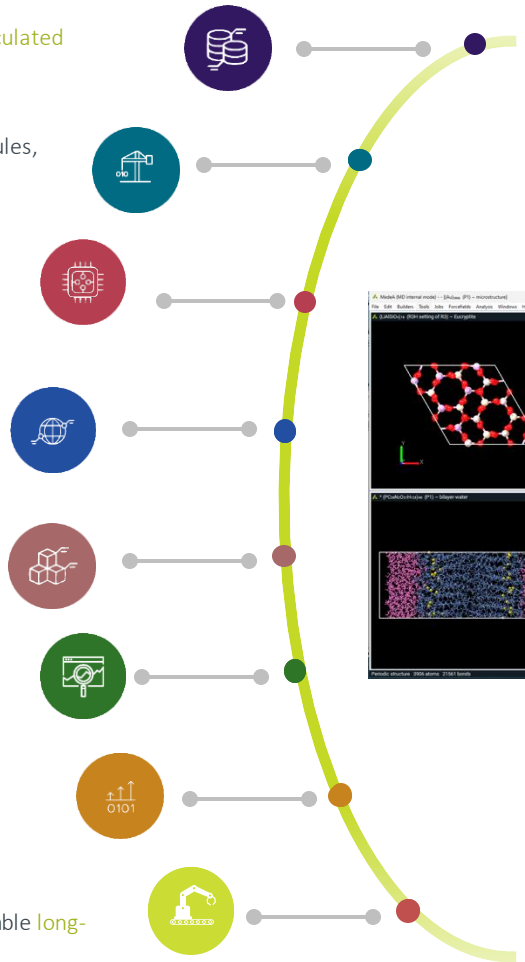
Generation of large and consistent sets of computed data & descriptors

Analysis Tools

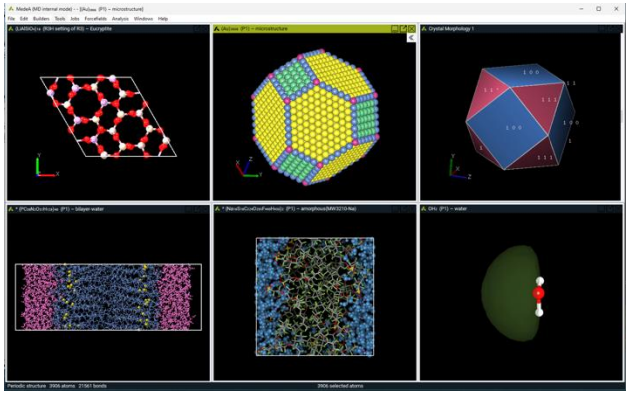
On-the-fly analysis, post-processing for system characterization and visualization, QSAR/QSPR

JobServer & TaskServer

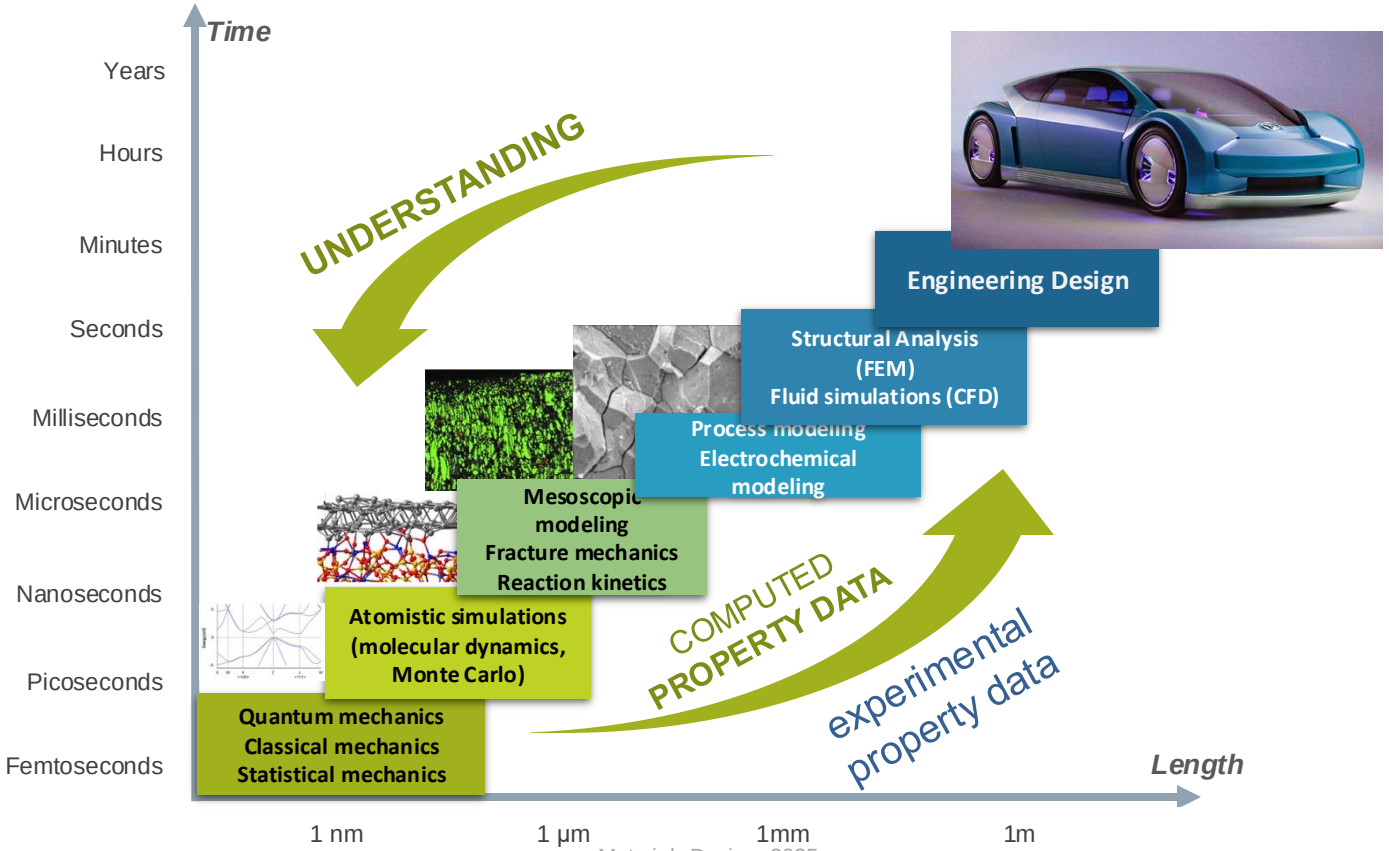
Automated processing of compute protocols & workflows; Reliable long-term archiving & accounting of computed data



MedeA



Value of Modeling and Simulation



materials design

Industrial questions related to:
Designing new & Optimizing existing Materials

- How can molecular simulation be used in applied R&D to assist with:
  - The designing of new materials?
  - The optimization of existing materials?
  - Quickly screening a list of candidate materials?
  - The understanding of observed behavior of materials?
- Which length and time scales are accessible?
- What are the requirements for using molecular modeling for daily operations in the industry?
- What is the level of expertise required to work with molecular modeling?

Building models of polymers for performing molecular simulations

- Bulk
- Surface models / slabs
- Composites
- Semi-crystalline
- Thermosets
- Atomistic / Coarse-grained

Generating Polymeric Systems

The use of **a realistic initial model**, whether it is a bulk or a slab, is a fundamental requirement in simulations for accurate property prediction

Many realistic initial models are required for **appropriate sampling** of configuration space and efficient property prediction

The **reduction of manual steps** for generating many realistic amorphous systems results in a reduction of errors and less time spent on tedious/repetitive tasks

Reusable workflows allow for consistent building and simulating processes which can easily be shared

Building models

A model is like a map. It provides a simplified representation of a complex reality.

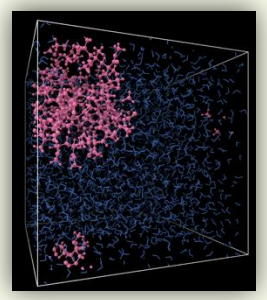
This simplification allows us to understand, predict, and control its properties more effectively.

The use of **a realistic initial model**, whether it is a bulk or a slab, is a fundamental requirement simulations for accurate property prediction

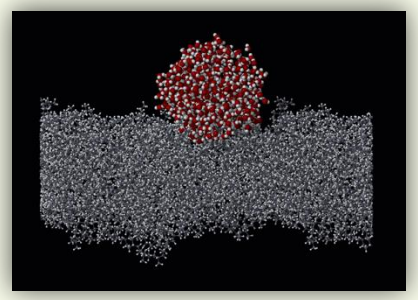
Many realistic initial models are required for **appropriate sampling** of configuration space and efficient property prediction

The **reduction of manual steps** for generating many realistic amorphous systems results in a reduction of errors and less time spent on tedious/repetitive tasks

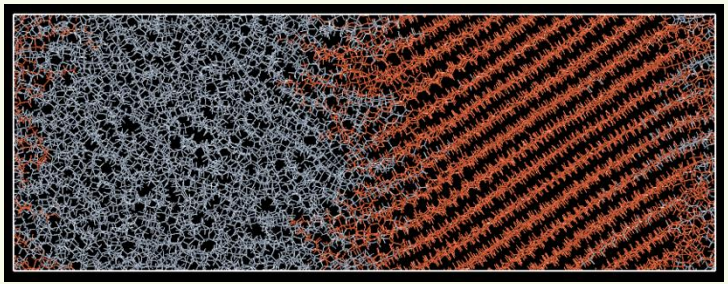
Reusable workflows allow for consistent building and simulating processes which can easily be shared



Polymer in water



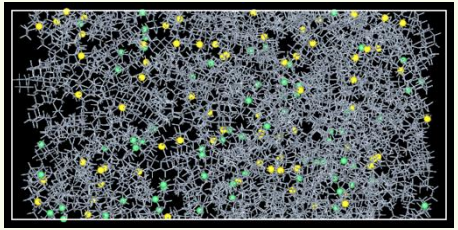
Water droplet on PP



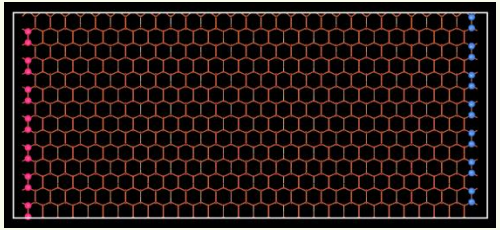
Semi-crystalline PE

Building a semi-crystalline polymer system (PE)

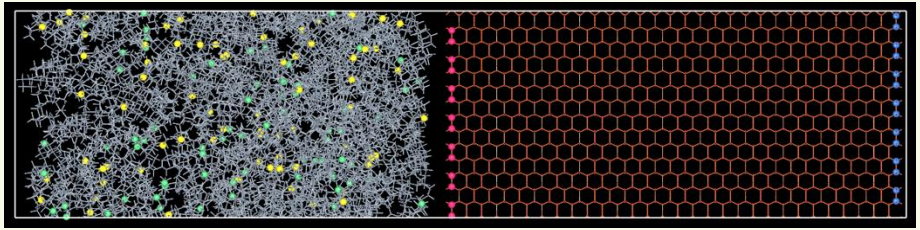
Create an amorphous region



Create a crystalline region

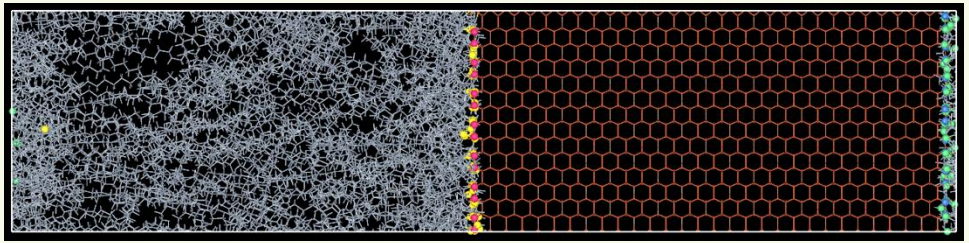


Stack the two regions

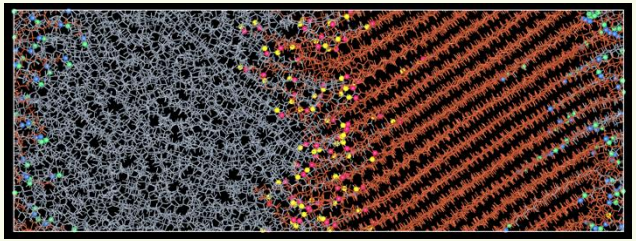


Highlighted atoms depict the chain ends, which will be used to connect the amorphous and crystalline phases

Connect the two regions



Equilibrate



CC/115902

Webinars:
1) Sorption and Diffusion of Small Gas Molecules in Semicrystalline Models: a Molecular-Scale Investigation,
2) Advancing Molecular-Scale Modeling: A Novel Approach for Semicrystalline Polymers

Belin et al., J. Phys. Chem. B 126, p. 9673-9685 (2022)

Building multiple models

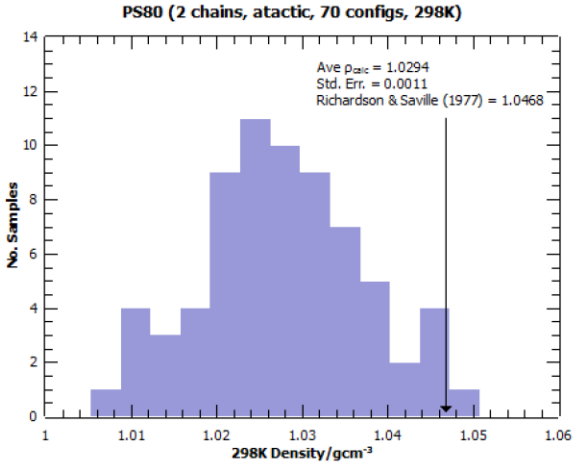
- Sampling is crucial for determining the sensitivity of the method and the expected accuracy
- Multiple simulation jobs starting from independent initial configurations are required to allow for the accurate calculation of the desired properties

The use of **a realistic initial model**, whether it is a bulk or a slab, is a fundamental requirement in simulations for accurate property prediction

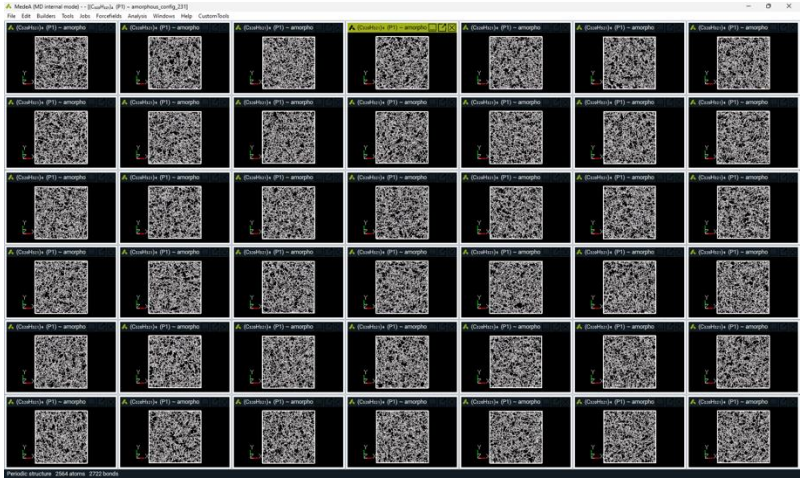
Many realistic initial models are required for **appropriate sampling** of configuration space and efficient property prediction

The **reduction of manual steps** for generating many realistic amorphous systems results in a reduction of errors and less time spent on tedious/repetitive tasks

Reusable workflows allow for consistent building and simulating processes which can easily be shared



PS80 (2 chains, atactic)



Building multiple models

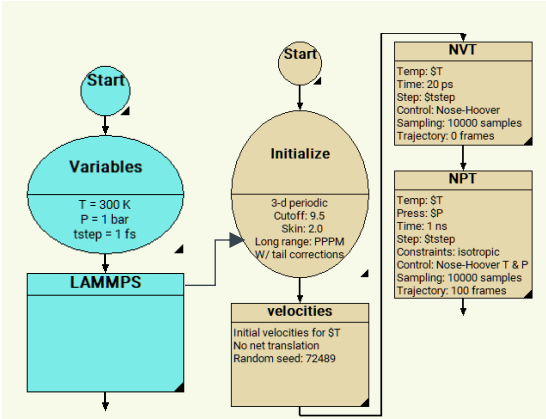
- Creation of a workflow, including various building stages
- High-Throughput mode use of workflows
- Facilitate collaboration by exchanging workflows

The use of **a realistic initial model**, whether it is a bulk or a slab, is a fundamental requirement in simulations for accurate property prediction

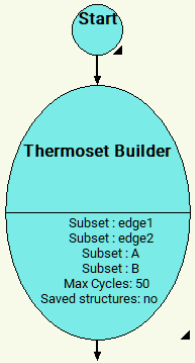
Many realistic initial models are required for **appropriate sampling** of configuration space and efficient property prediction

The **reduction of manual steps** for generating many realistic amorphous systems results in a reduction of errors and less time spent on tedious/repetitive tasks

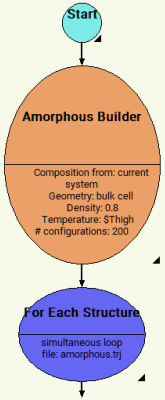
Reusable workflows allow for consistent building and simulating processes which can easily be shared



Generation of an MD trajectory



Generation of crosslinked models



Generation of amorphous models

Property prediction on built models

Accurate Property Prediction

Realistic polymer models can provide more accurate predictions of properties such as mechanical strength, thermal conductivity, and gas permeability.

Enhanced Understanding of Material Behavior

These models can help researchers understand the underlying molecular mechanisms that govern material behavior, leading to improved design and optimization.

Efficient Material Development

By simulating the properties of various polymer structures, researchers can identify promising candidates for new materials, while minimizing the need for costly and time-consuming experiments.

Tailored Material Design

Realistic models allow for the design of materials with specific properties, such as high-performance polymers for aerospace or biocompatible materials for medical applications.

Process Optimization

Understanding the molecular structure and behavior of polymers can lead to more efficient manufacturing processes and reduced waste.

Pure Polymer Properties			
1	Density	9	Heat capacity
2	Molar volume	10	Hildebrand Solubility parameter
3	Cohesive Energy Density	11	Glass transition temperature
4	Heat Capacity	12	Poisson's ratio
5	Thermal Conductivity	13	Bulk modulus
6	Surface energy	14	Young's modulus
7	Surface tension	15	Shear modulus
8	Thermal expansion coefficient	16	Entanglement molecular weight

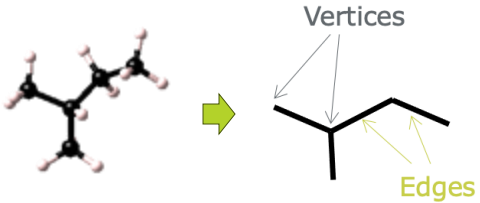
Multi-component Properties (fluids & Polymers)			
1	Density	8	Permeability
2	Henry Solubility Constant	9	Contact angles / wetting
3	Thermal Conductivity	10	Swelling
4	Elastic moduli	11	Interfacial tension
5	Gel point	12	Porosity (pyknometry)
6	Sorption / solubility	13	Surface Area (BET, Langmuir)
7	Diffusivity		

Webinar: Use of Polymer Theoretical Concepts in Atomistic Polymer Simulation Software

Polymer Property Prediction using Correlations – P3C

Validated correlations based on topological indices

Hydrogen-suppressed graph of molecules

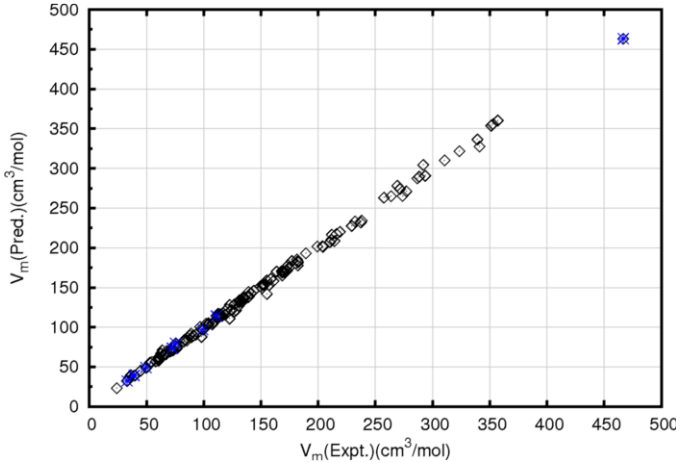


Prediction of Polymer Properties (Third Edition), Jozef Bicerano, Marcel Dekker, Inc., 2002

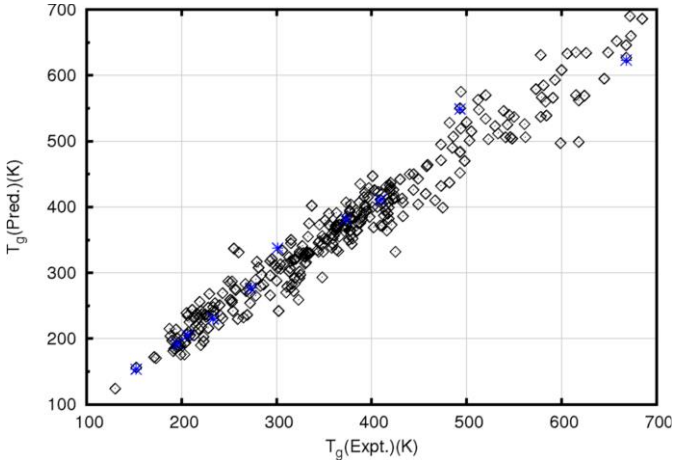
- A **property** is calculated from a **correlation**:
  - based on **connectivity indices**
  - augmented with **correction terms** relating to key features contained within constituent repeat units (atomic and group correction terms dependent upon the number of certain types of atoms or groups that may be present)

- **Designer correlations** are improved correlations highly **tuned to specific systems**
  - not widely applicable
  - once such correlations have been established, they may be employed to generate property data for novel repeat units

V_m and T_g from P3C



Comparison of experimental and predicted molar volumes, V_m, for 152 polymers as reported by Bicerano (◊). MedeA® Polymer Property value results are shown (+) for a selection of systems .



Comparison of experimental and predicted glass transition temperatures for 320 polymers as reported by Bicerano (◊). Selected MedeA® Polymer Property values are shown in +.

Prediction of Polymer Properties (Third Edition), Jozef Bicerano, Marcel Dekker, Inc., 2002

Property prediction using high-quality correlations

Rapid & Easy Application

Correlations provide a quick and efficient way to estimate polymer properties, aiding in screening large arrays of polymers and focusing simulations and experiments.

Wide Applicability

Correlations can be used to predict properties for a wide range of homopolymers and copolymers, making them valuable tools for screening and preliminary assessments.

Accurate Predictions

High-quality correlations are developed based on extensive experimental data and can provide reliable estimates of properties such as glass transition temperature, melting point, and solubility.

Cost effective

Using correlations can significantly reduce the time and resources required for property prediction compared to experimental methods, making them a cost-effective option.

Thermophysical	
1	Glass transition temperature, Tg
2	Temperature of half decomposition
3	Change in molar heat capacity at Tg
4	Coefficient of volumetric thermal expansion
5	Cohesive energy
6	Cp of liquid
7	Cp of solid
8	Density
9	Molar volume
10	Solubility parameter
11	Surface tension
12	van der waals volume
13	Thermal conductivity

Entanglement	
1	Entanglement molecular weight
2	Entanglement length
3	Critical molecular weight
4	Steric hinderance parameter
5	Characteristic ratio
6	Molar stiffness function
7	Additive portion of molar viscosity-temperature function
8	Activation energy for viscous flow at zero flow rate

Mechanical	
1	Brittle fracture stress
2	Bulk modulus
3	Poisson's ratio
4	Shear modulus
5	Shear yield stress
6	Young's modulus

Transport	
1	Permeability to CO_2, N_2 and O_2
2	Zero-shear viscosity
3	Diffusion coefficients for N_2 and O_2

Electronic & optical	
1	Diamagnetic susceptibility
2	Dielectric constant
3	Molar refraction
4	Refractive index
5	Volume resistivity

Computer Aided Molecular Design – Polymer Expert

Example: Identifying possible candidates for creating straws of smaller environmental footprint

Straws

The global drinking straw market is valued at an astonishing 25 billion dollars per annum

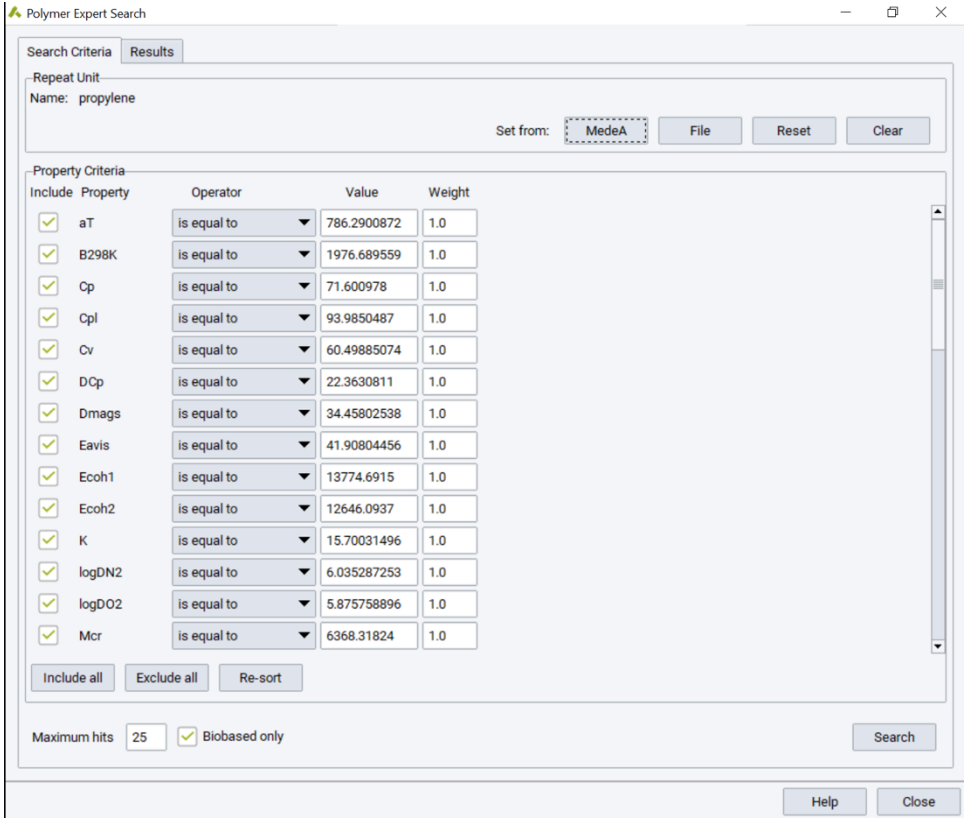
The problem:

- PP is inexpensive and produces a robust product but survives in the environment for decades, releasing harmful chemicals during decomposition

The solution:

- Identifying alternatives with similar physicochemical properties and a lower environmental impact

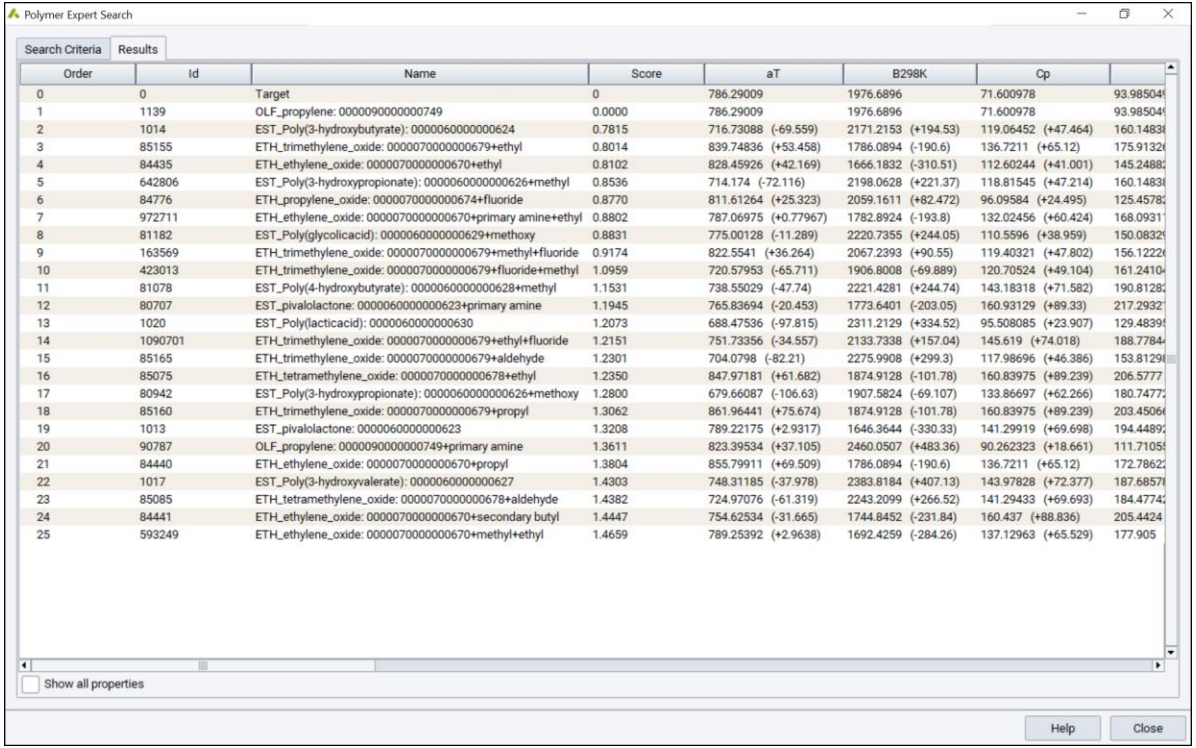
Identify potential candidates



- Define the Repeat Unit of the polymer, the properties of which may be used as a reference
- Choose which Properties should be used as criteria for searching the database (containing ~1 million repeat units), their values and their weight; choose whether only biobased materials are of interest
- Search the database for potential candidates

Potential candidates identified

- Using knowledge-augmented machine learning, *MedeA Property Expert* takes supplied properties and provides candidate polymers which are capable of providing those desired characteristics
- The first and second hits are polypropylene and polyhydroxybutyrate (PHB) respectively, and polylactic acid is hit number 13



Order	Id	Name	Score	aT	B298K	Cp	
0	0	Target	0	786.29009	1976.6896	71.600978	93.98504
1	1139	OLF_propylene: 0000090000000749	0.0000	786.29009	1976.6896	71.600978	93.98504
2	1014	EST_Poly(3-hydroxybutyrate): 0000060000000624	0.7815	716.73088 (-69.559)	2171.2153 (+194.53)	119.06452 (+47.464)	160.1483
3	85155	ETH_trimethylene_oxide: 00000700000000679+ethyl	0.8014	839.74836 (+53.458)	1786.0894 (-190.6)	136.7211 (+65.12)	175.9132
4	84435	ETH_ethylene_oxide: 0000070000000670+ethyl	0.8102	828.45926 (+42.169)	1666.1832 (-310.51)	112.60244 (+41.001)	145.2488
5	642806	EST_Poly(3-hydroxypropionate): 0000060000000626+methyl	0.8536	714.174 (-72.116)	2198.0628 (+221.37)	118.81545 (+47.214)	160.1483
6	84776	ETH_propylene_oxide: 0000070000000674+fluoride	0.8770	811.61264 (+25.323)	2059.1611 (+82.472)	96.09584 (+24.495)	125.4578
7	972711	ETH_ethylene_oxide: 0000070000000670+primary amine+ethyl	0.8802	787.06975 (+0.77967)	1782.8924 (-193.8)	132.02456 (+60.424)	168.0931
8	81182	EST_Poly(glycolicacid): 0000060000000629+methoxy	0.8831	775.00128 (-11.289)	2220.7355 (+244.05)	110.5596 (+38.959)	150.0832
9	163569	ETH_trimethylene_oxide: 00000700000000679+methyl+fluoride	0.9174	822.5541 (+36.264)	2067.2393 (+90.55)	119.40321 (+47.802)	156.1222
10	423013	ETH_trimethylene_oxide: 00000700000000679+fluoride+methyl	1.0959	720.57953 (-65.711)	1906.8008 (-69.889)	120.70524 (+49.104)	161.2410
11	81078	EST_Poly(4-hydroxybutyrate): 0000060000000628+methyl	1.1531	738.55029 (-47.74)	2221.4281 (+244.74)	143.18318 (+71.582)	190.8128
12	80707	EST_pivalolactone: 0000060000000623+primary amine	1.1945	765.83694 (-20.453)	1773.6401 (-203.05)	160.93129 (+89.33)	217.2932
13	1020	EST_Poly(lacticacid): 0000060000000630	1.2073	688.47536 (-97.815)	2311.2129 (+334.52)	95.508085 (+23.907)	129.4839
14	1090701	ETH_trimethylene_oxide: 00000700000000679+ethyl+fluoride	1.2151	751.73356 (-34.557)	2133.7338 (+157.04)	145.619 (+74.018)	188.7784
15	85165	ETH_trimethylene_oxide: 0000070000000679+aldehyde	1.2301	704.0798 (-82.21)	2275.9908 (+299.3)	117.98696 (+46.386)	153.8129
16	85075	ETH_tetramethylene_oxide: 0000070000000678+ethyl	1.2350	847.97181 (+61.682)	1874.9128 (-101.78)	160.83975 (+89.239)	206.5777
17	80942	EST_Poly(3-hydroxypropionate): 0000060000000626+methoxy	1.2800	679.66087 (-106.63)	1907.5824 (-69.107)	133.86697 (+62.266)	180.7477
18	85160	ETH_trimethylene_oxide: 0000070000000679+propyl	1.3062	861.96441 (+75.674)	1874.9128 (-101.78)	160.83975 (+89.239)	203.4506
19	1013	EST_pivalolactone: 0000060000000623	1.3208	789.22175 (+2.9317)	1646.3644 (-330.33)	141.29919 (+69.698)	194.4489
20	90787	OLF_propylene: 0000090000000749+primary amine	1.3611	823.39534 (+37.105)	2460.0507 (+483.36)	90.262323 (+18.661)	111.7105
21	84440	ETH_ethylene_oxide: 0000070000000670+propyl	1.3804	855.79911 (+69.509)	1786.0894 (-190.6)	136.7211 (+65.12)	172.7862
22	1017	EST_Poly(3-hydroxyvalerate): 0000060000000627	1.4303	748.31185 (-37.978)	2383.8184 (+407.13)	143.97828 (+72.377)	187.6857
23	85085	ETH_tetramethylene_oxide: 0000070000000678+aldehyde	1.4382	724.97076 (-61.319)	2243.2099 (+266.52)	141.29433 (+69.693)	184.4774
24	84441	ETH_ethylene_oxide: 0000070000000670+secondary butyl	1.4447	754.62534 (-31.665)	1744.8452 (-231.84)	160.437 (+88.836)	205.4424
25	593249	ETH_ethylene_oxide: 0000070000000670+methyl+ethyl	1.4659	789.25392 (+2.9638)	1692.4259 (-284.26)	137.12963 (+65.529)	177.905

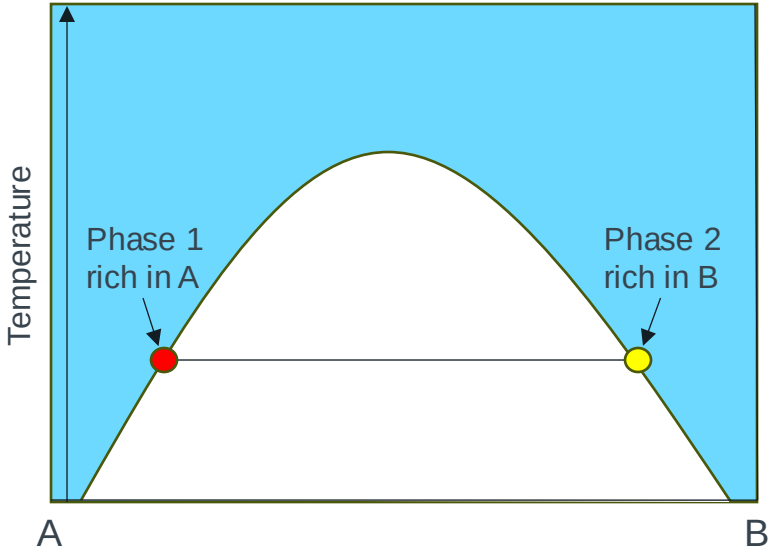
Designing new & Optimizing existing polymers

- **Targeted Material Design**: Knowledge-augmented machine learning (ML) algorithms can efficiently search through vast databases of polymers and their properties to identify candidates that meet specific criteria, accelerating the development of materials with desired characteristics.
- **Novel Material Discovery**: By exploring unconventional combinations of monomers and structural features, knowledge-augmented ML can uncover novel polymer structures that traditional design methods may not have considered.
- **Enhanced Efficiency**: Knowledge-augmented ML can significantly reduce the time and cost associated with experimental trials, allowing for more rapid development and optimization of new polymers.
- **Improved Property Prediction**: Knowledge-augmented ML models can be trained on large datasets of polymer properties to develop more accurate and reliable prediction models, supporting informed decision-making in material selection and design.
- **Complex Property Optimization**: Knowledge-augmented ML can handle complex property optimization problems involving multiple interdependent properties, enabling the design of materials with tailored combinations of characteristics.

Mesoscopic Polymer Modeling – PhaseField

Spinodal decomposition

Spinodal Decomposition

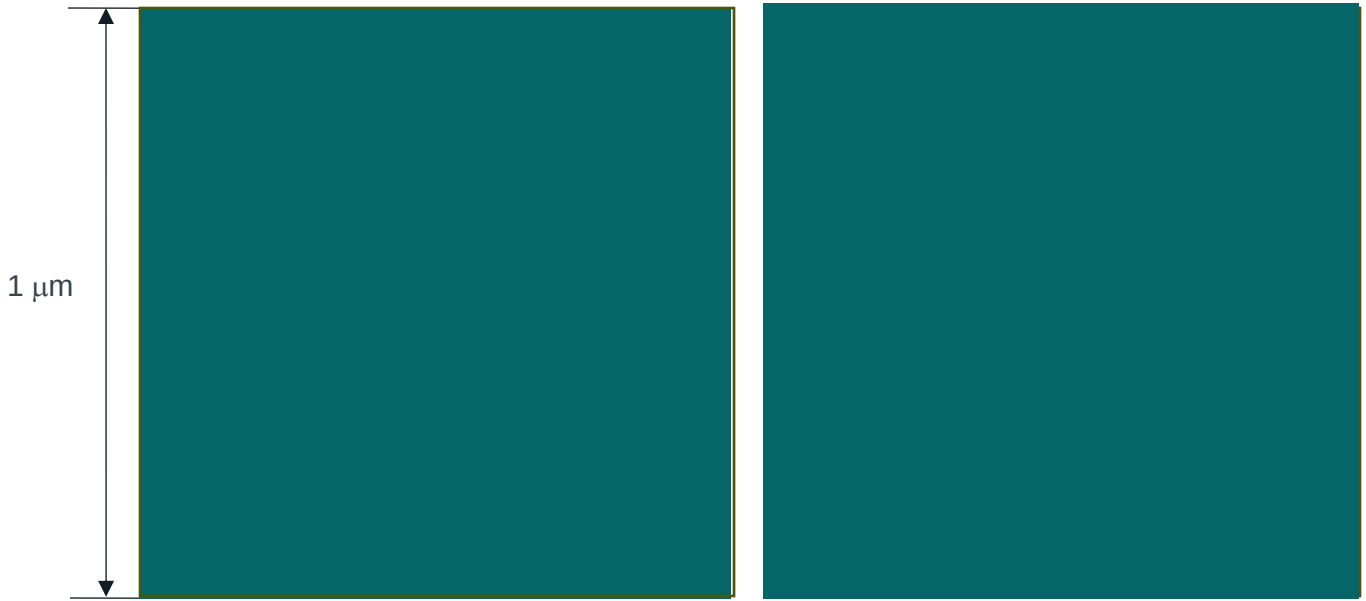


- The phase separation is without a barrier and does not require nucleation.
- What properties like the interface energy between separated phases determine the resulting morphology?

Spinodal Decomposition

Lower interface energy leads to larger interface area

Higher interface energy leads to less interface area



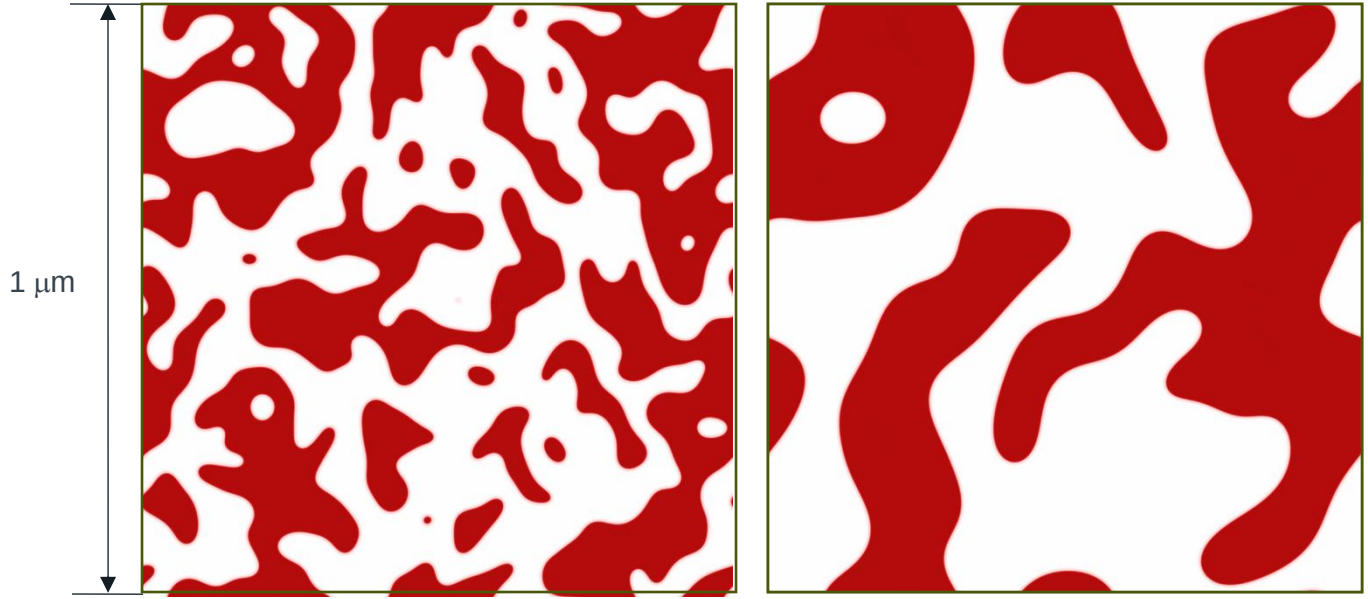
Interface energies: **1 J/m^2**
Diffusion coefficients: 1.0 $\times 10^{-14}$ cm^2/s
Duration: 365 days
Job: D172751

Interface energies: **7 J/m^2**
Diffusion coefficients: 1.0 $\times 10^{-14}$ cm^2/s
Duration: 365 days
Job: D172755

Spinodal Decomposition

Lower interface energy leads to larger interface area

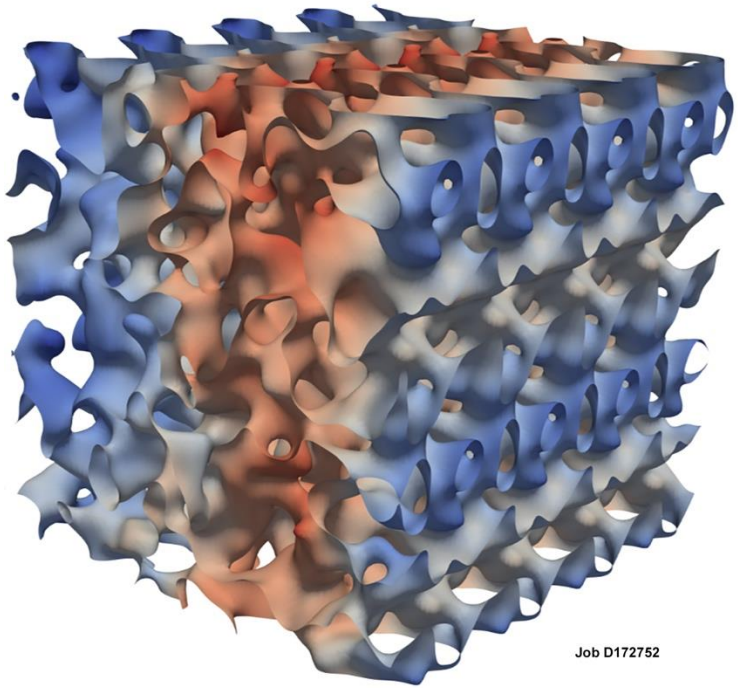
higher interface energy leads to less interface area



Interface energies: **1 J/m^2**
Diffusion coefficients: 1.0 $\times 10^{-14}$ cm^2/s
Duration: 365 days
Job: D172751

Interface energies: **7 J/m^2**
Diffusion coefficients: 1.0 $\times 10^{-14}$ cm^2/s
Duration: 365 days
Job: D172755

Spinodal Decomposition – 3D



Dimension of simulation cell: 0.5×0.5×0.5 μm

Duration: 100 days

$$E = \tfrac{1}{2} k \left(c - c_0 \right)^2 + E_0$$

Free energy vs. concentration and diffusion:

liquid: k=1.0, c_0 = 0.5, E_0 = 0.0 eV/Å^3, D=1.0 ×10^{-12} cm^2/s

solid1: k=1.0, c_0 = 0.25, E_0 = -0.1 eV/Å^3, D=1.0 ×10^{-12} cm^2/s

solid2: k=1.0, c_0 = 0.75, E_0 = -0.1 eV/Å^3, D=1.0 ×10^{-12} cm^2/s

Interface energies: all 1 J/m^2

Interface mobility: all 1.0 ×10^{-23}m^4/(Js)

Polymers & Phase Field simulations

- **Microscopic Structure Prediction**: Phase field simulations can predict the microstructure of polymers at a mesoscale level, providing insights into phase separation, domain formation, and interfacial properties.
- **Time and length scales**: Phase field simulations allow the extension of length and time scales to µm and months/years.
- **Morphological Evolution**: These simulations can track the evolution of polymer morphology over time, allowing for the study of processes like phase transitions and ageing.
- **Multicomponent Systems**: Phase field simulations can handle complex multicomponent polymer systems, making them suitable for studying blends, copolymers, and composite materials.
- **Input for Phase Field modeling**: Input parameters for Phase Field simulations can be derived from atomistic simulations.

Summary

- Models:
  - Creating **well-defined** and **realistic models** is essential for accurate property prediction in molecular simulations
  - Employing many **independent initial configurations** in simulations enhances statistical sampling and **improves property predictions**
- Workflows:
  - **Automated workflows** streamline the simulation process by providing **consistent** and **user-friendly protocols** ready to be applied
  - **Automated workflows** reduce manual effort and repetitive tasks, leading to **increased productivity**
  - The ability to **save, share, and retrieve simulation workflows** promotes **reproducibility** and **consistency** in computational studies

Conclusions

- Molecular simulations provide **valuable insight** into polymer properties and behavior, enabling **accurate predictions** and a **deeper understanding** of polymer-containing systems
- **Reliable property prediction** methods are increasingly being **integrated into industrial R&D workflows** to support material development and optimization
- **Combining molecular simulations with correlations, AI-driven CAMD, and Phase Field modeling** provides a **comprehensive understanding** of materials and their properties
- A **multi-scale** approach, where information from lower-level simulations is used to inform higher-level simulations, enables **consistent modeling across length and time scales**
- **Advanced automation** and **built-in safeguards** in molecular modeling tools make them **accessible** to users with **varying levels of expertise**

Thank you!

Related *MedeA* Webinars

Sorption and Diffusion of Small Gas Molecules in Semicrystalline Models: a Molecular-Scale Investigation

https://www.materialsdesign.com/webinars/recorded/sorption-and-diffusion-of-small-gas-molecules-in-semicrystalline-models%3A-a-molecular-scale-investigation

Advancing Molecular-Scale Modeling: A Novel Approach for Semicrystalline Polymers

https://www.materialsdesign.com/webinars/recorded/advancing-molecular-scale-modeling-a-novel-approach-for-semicrystalline-polymers

materials design

Highlighted *MedeA* Modules

MedeA Environment

MedeA Amorphous Materials Builder

MedeA Thermoset Builder

MedeA VASP

MedeA LAMMPS

MedeA GIBBS

MedeA GAUSSIAN

MedeA MOPAC

MedeA MLP

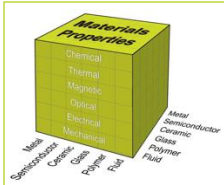
MedeA MLPG

MedeA P3C

MedeA Polymer Expert

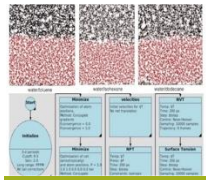
MedeA High Throughput

MedeA PhaseField



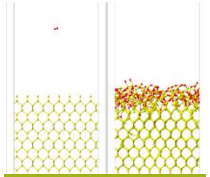
MedeA Environment

Atomistic Modeling and Simulation environment



Transport

Diffusion, Viscosity, Thermal conductivity, Surface Tension



Deposition,

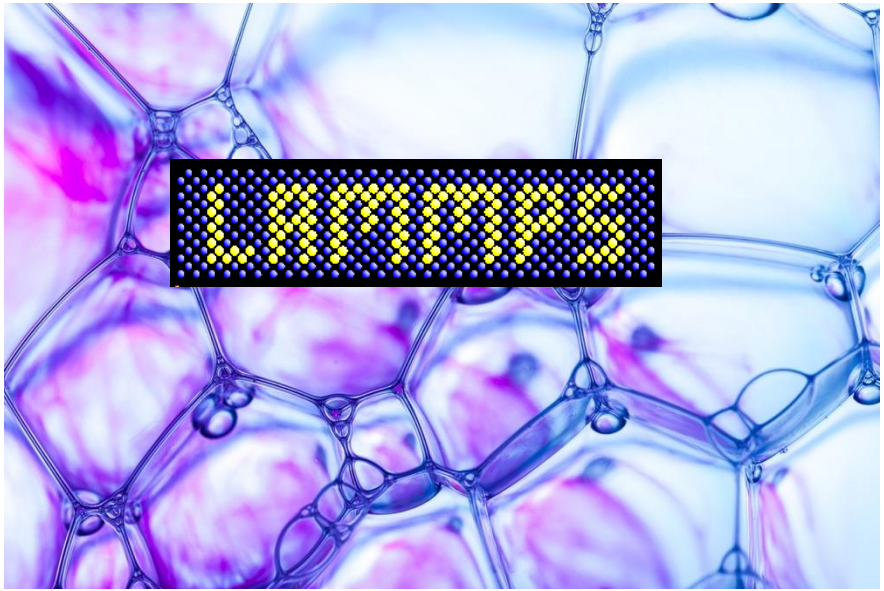
Growth, Oxidation, and Etching

materials design

materials design

MedeA LAMMPS Training

Dr. Garrett Tow and the MD Support Team



Date: February 13, 2025

Time: 8 am PST / 11 am EST / 5 pm CET

Duration: 4 hours (including breaks and Q&A sessions)

Platform: Virtual only (details will be provided upon registration)

You'll Receive:

- Access to comprehensive training materials.
- Live demonstrations and hands-on practice sessions.
- Expert guidance from seasoned professionals.
- 14-day evaluation license for *MedeA LAMMPS* to continue your exploration after the live session.

Question and Answer Session

Marianna Yiannourakou

Materials Design

David Rigby

Materials Design

Benoit Minisini

Materials Design

Questions about Materials Design Webinars

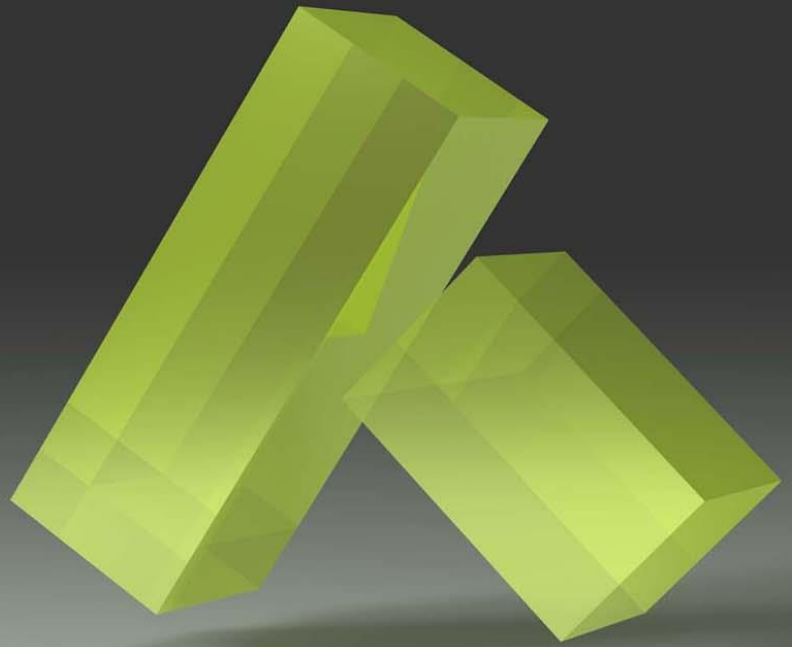
Katherine Hollingsworth

khollingsworth@materialsdesign.com

materials design

info@materialsdesign.com

www.materialsdesign.com



MedeA

Innovation by Simulation