Polymers in Soft Matter: From Structure to Emerging Applications

Part 3: Emerging Applications and Techniques

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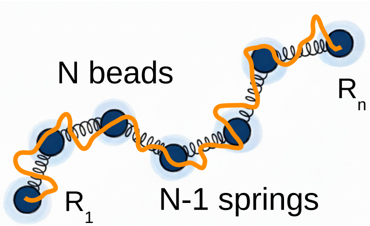
INNANOMAT MATERIALS FOR INNOVATION

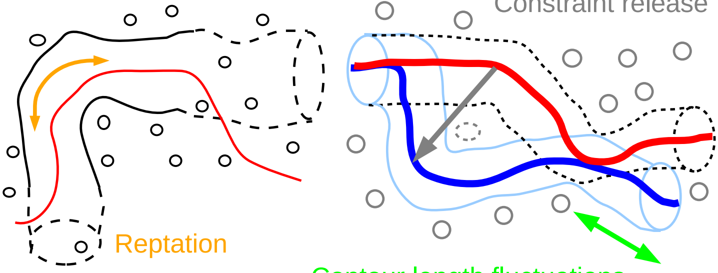
Rouse and Zimm model

- bead-spring representation
- beads with identical friction coefficient ζ



- Zimm: $\tau_Z \propto N^{3\nu}$ ($\nu \approx 0{,}588$ in good solvent $\Longrightarrow N^{1{,}764}$)
- Rouse: $\tau_R \propto N^2$
- Zimm: $D_{cm} \propto N^{-\nu}$ (i.e., $N^{-0{,}588}$ in good solvent)
- Rouse: $D_{cm} \propto N^{-1}$
- Zimm: $\eta \propto N^{3\nu-1}$ (i.e., $N^{0{,}754}$ in good solvent)
- Rouse: $\eta \propto N^1$

Tube model



- relaxation time: $\tau_d \propto N^3$
- diffusion coefficient: $D_{cm} \propto N^{-2}$
- viscosity $\eta \propto N^3$

! $3 \longrightarrow 3.4$, $2 \longrightarrow 2.3$

Summary of the methods for dynamical properties

- rheology (oscillatory shear): viscosity, plateau modulus (tube model parameters), wide spectrum of the relaxation times
- microrheology: MSD and viscoelastic properties
- dielectric spectroscopy: segmental motion
- neutron spin echo: tube model parameters, segmental motion, MSD
- nuclear magnetic resonance: local motion (ns-μs)
- differential scanning calorimetry: glass transition temperature
- fluorescence correlation spectroscopy: diffusion coefficient
- molecular dynamics simulations

Polymers at interfaces

Interface: 2D boundary solid/liquid, liquid/gas, solid/solid
Interphase: 3D region with different properties than the bulk

A: Polymer-Solid Interfaces

- supported films, nanocomposites, matrix+fibers

B: Polymer-Liquid Interfaces

- hydrogels, membranes, polymer brushes

C: Polymer-Gas Interfaces

- gas barrier films, superhydrophobic coatings

D: Polymer-Polymer Interfaces

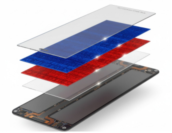
- polymer blends, multilayers

A

B

C

D

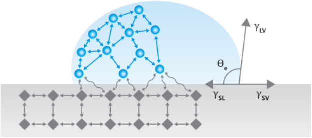


Surface free energy (SFE) of polymers

- painting, printing, coatings, wetting phenomena, biomaterial–cell interactions

SFE:

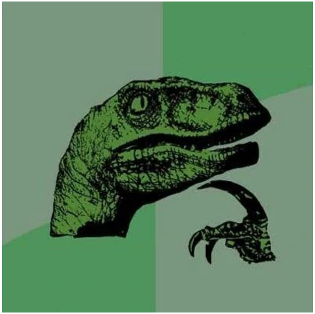
- measuring the contact angle of several probe liquids
- SFE divided into individual components containing dispersion forces and polar/hydrogen-bonding forces



$$\gamma = \gamma_\infty - KM^{-\alpha}, \quad \alpha = 1, 2/3$$

low SFE: polyethylene (food packaging), polydimethylsiloxane (superhydrophobic surfaces)

[1] Susanna Lauren, Biolin Scientific: Surface free energy – what is it and how to measure it?

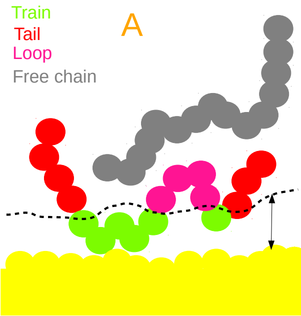


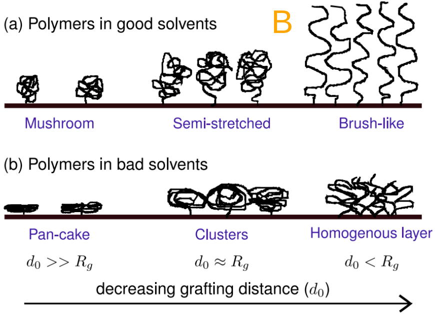
Tell me one industrial polymer well-known for its low surface energy.

Polymer chain conformation at interfaces

A physical adsorption in polymer films

B chemical adsorption in brushes

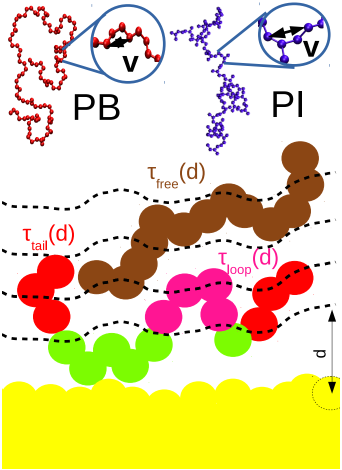


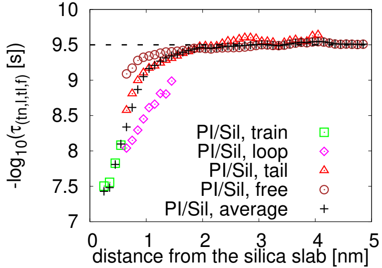


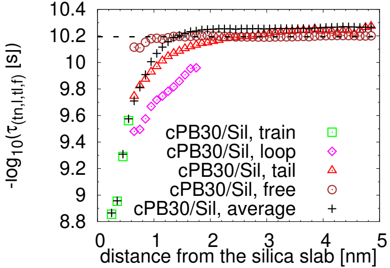
⇒ non-uniform density profile

[1] Singh, M.K. (2020). Polymer Brush Based Tribology. In: Katiyar, J., Ramkumar, P., Rao, T., Davim, J. (eds) Tribology in Materials and Applications. Materials Forming, Machining and Tribology. Springer

Polymer dynamics at interfaces







[1] Bačová P, Li W, Behbahani AF, Burkhart C, Polińska P, Doxastakis M, Harmandaris V., Nanomaterials. 2021; 11(8), 2075

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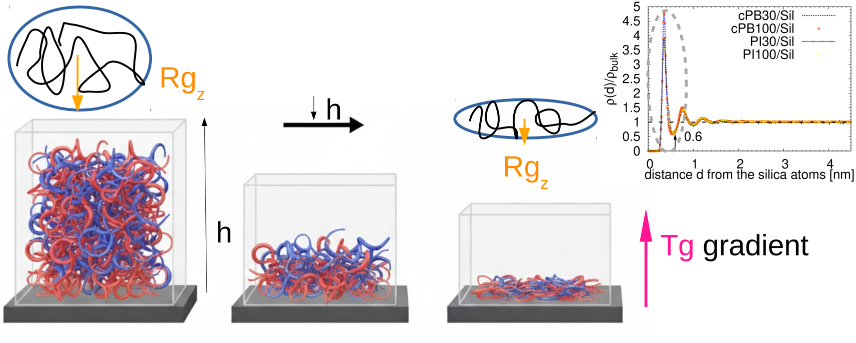
INNANOMAT MATERIALS FOR INNOVATION

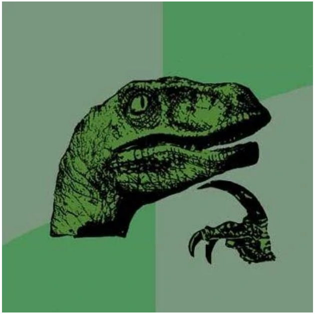
Polymer thin films

- up to 200 μm thick, thicker=sheets
- extrusion, film casting, calandering, extrusion coating

Confinement effects

- R_g vs. h: chain rigidity dependent





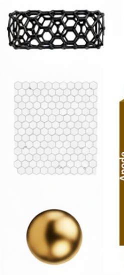
Guess the method of production of garbage bags.

Polymer nanocomposites

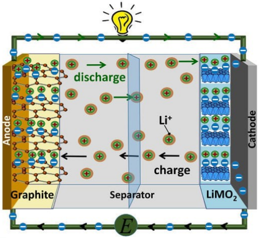
- composite materials, nanofillers in a polymer matrix
- enhanced properties with low loading of filler, improvement dependent on the polymer-surface interactions

Nanofillers:

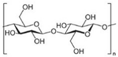
- fibers, tubes, platelets, sheets, particles
- carbon-based, silica-based, metals, ceramics, bio-based, all-polymer

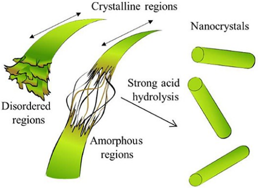


TiO2-based electrodes



nanocellulose

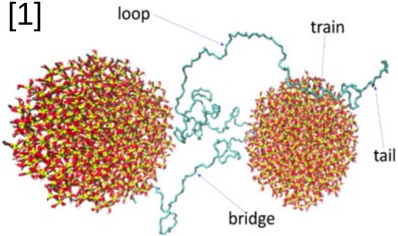


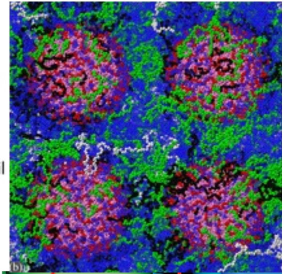


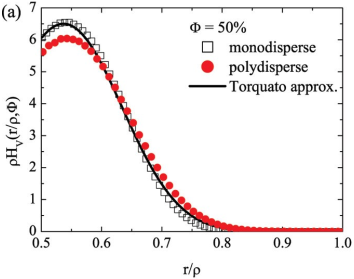
[1] Trache D., et. al. (2020) Front. Chem. 8:392
[2] Madian, M.; Eychmüller, A.; Giebeler, L.; Batteries 2018, 4, 7.

Bare nanoparticles

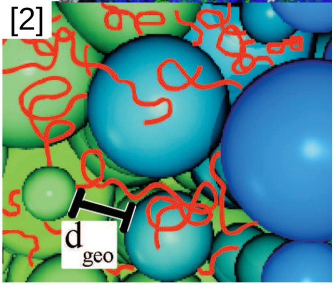
[1]







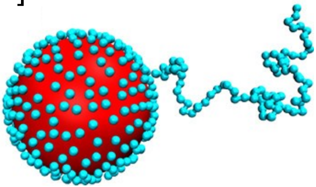
[2]

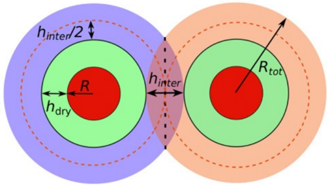


[1] A. F. Behbahani, et. al., Macromolecules, 2020, 53 (15), 6173-6189
[2] G. J. Schneider, K. Nusser, L. Willner, P. Falus, D. Richter, Macromolecules, 2011, 44 (15), 5857-5860

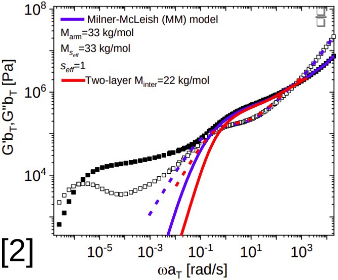
Grafted nanoparticles

[1]

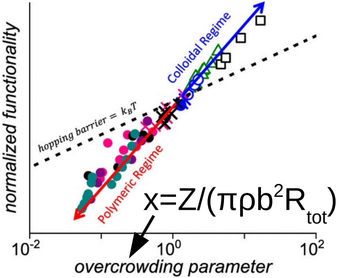




Two-layer model

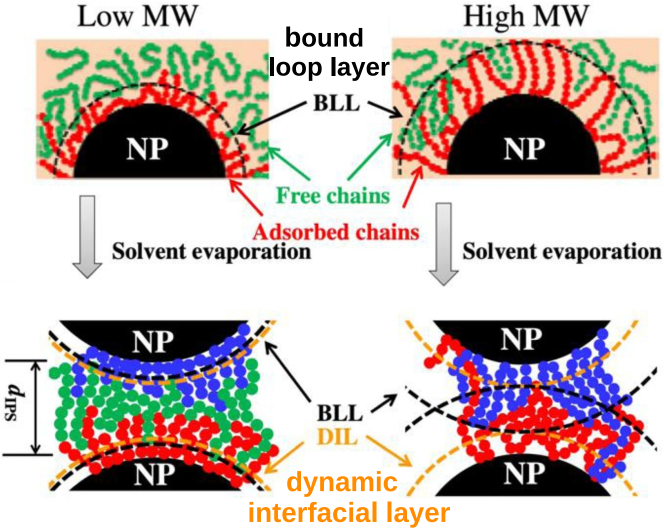


[2]



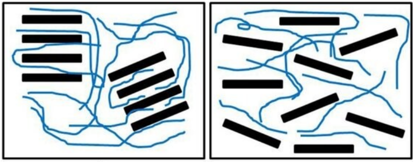
[1] J. Midya, M. Rubinstein, S. K. Kumar, A. Nikoubashman, ACS Nano, 2020, 14 (11), 15505-15516
[2] D. Parisi et al., ACS Nano, 2021, 15 (10), 16697-16708

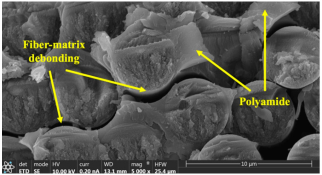
Other theoretical approaches



[1] S. Cheng et al., Phys. Rev. Lett., 2016, 116, 038302

The challenges of hybrid materials





Filler-matrix compatibility:

- essentiaal for good mechanical properties
- debonding

Nanofiller dispersion:

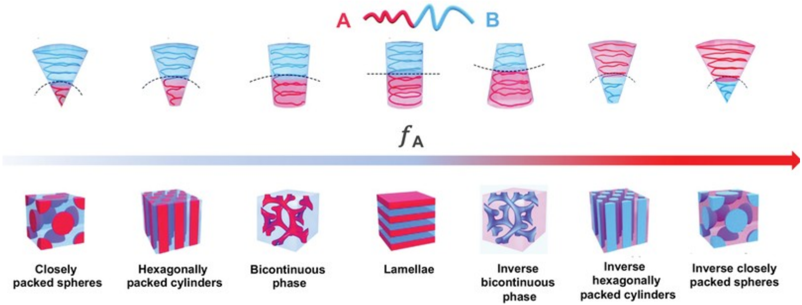
- maximizes the total filler-matrix interfacial area
- aggregation decreases the enhancement
- surface modification: coupling agents, surfactants

+processability
+cost and environmental impact

[1] Wang, Mingchao; Yan, Cheng; Ma, Lin. (2012). Graphene Nanocomposites. 10.5772/50840.
[2] Butenegro, J.A. et al., Polymers, 2023, 15, 3447

Advanced films: block copolymer self-assembly

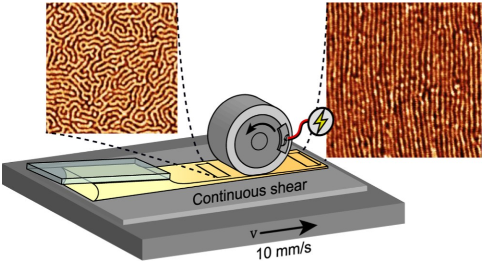
- spontaneous microphase separation at the order–disorder transition temperature
- driven by chemical dissimilarity, formation of nanoscale morphologies
- factors: Flory-Huggins interaction parameter, molecular weight, architecture, temperature, surface properties, external field etc.

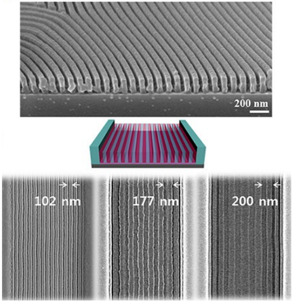


[1] L. Xiang, Q. Li, C. Li, Q. Yang, F. Xu, Y. Mai, Adv. Mater. 2023, 35, 2207684.

Advanced films: block copolymer self-assembly

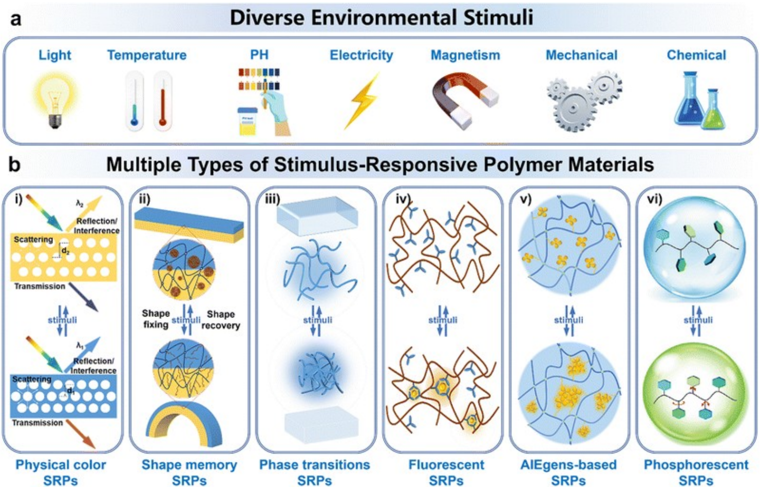
- spin-coating, dip-coating, electrospray deposition, post-shear annealing, solvent vapor-assisted graphoepitaxial ordering
- optical coatings, metamaterials, plasmonic nanostructures, membranes





[1] E. R. Gottlieb et al., ACS Applied Polymer Materials, 2022 4 (1), 682-691.
[2] E. Kim, et al., ACS Nano, 2013, 7 (3), 1952-1960.

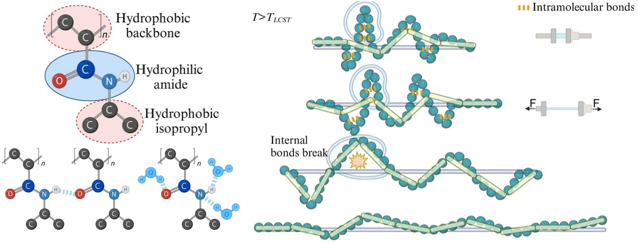
Stimuli-responsive materials

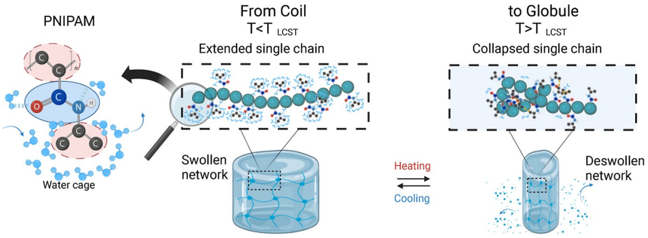


[1] Y. Shen , X. Le , Y. Wu and T. Chen , Chem. Soc. Rev., 2024, 53 , 606 —623

PNIPAM gels

- poly(N-isopropylacrylamide)
- tissue engineering, drug delivery systems, soft robotics





[1] Michal Levin and Noy Cohen,
Macromolecules, 2025, 58 (10), 5187-5200

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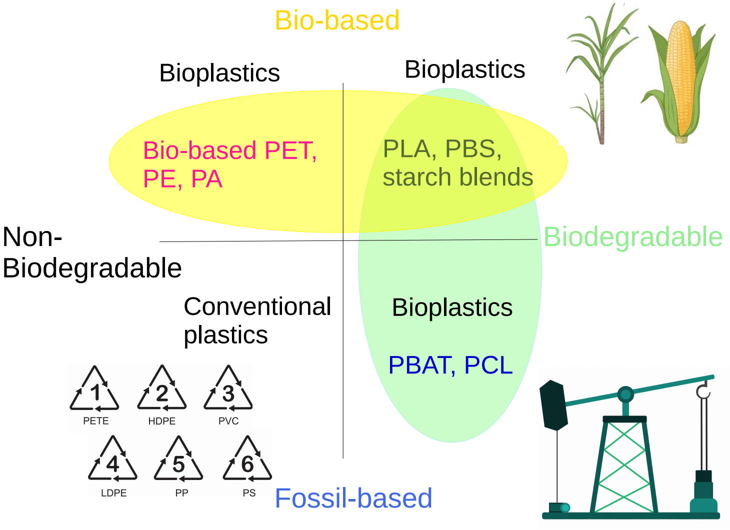
INNANOMAT MATERIALS FOR INNOVATION

Sustainable polymers



Design by Vecteezy/ BioRender

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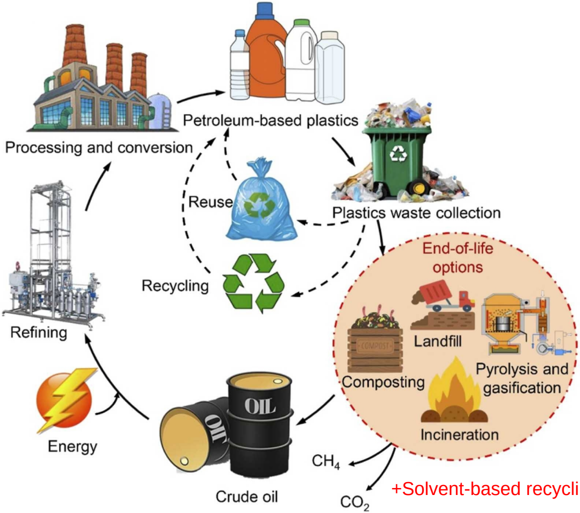
INNANOMAT MATERIALS FOR INNOVATION

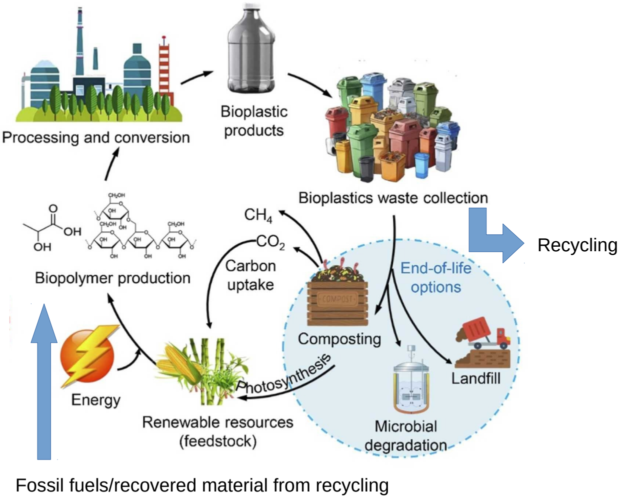
Life cycle of conventional plastics



+Solvent-based recycling

H. Jiao et al., Ecotoxicology and Environmental Safety, 271, 2024, 115942

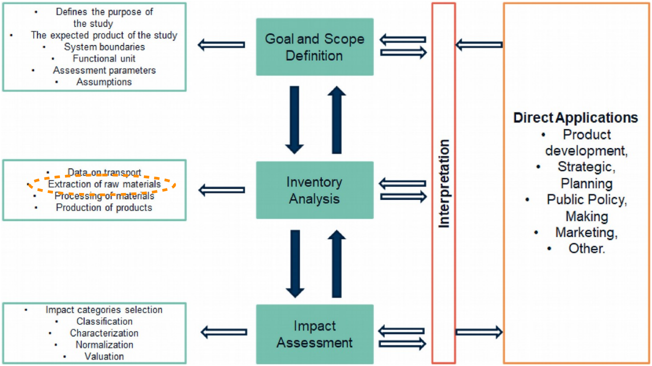
Life cycle of bioplastics



H. Jiao et al., Ecotoxicology and Environmental Safety, 271, 2024, 115942

Life cycle assesment (LCA) of plastics

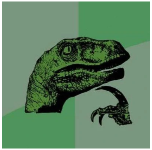
ISO 14040:



- use-phase benefits (prevented food losses, lightweighting, protection of durable goods)
- non-climate environmental impacts: eutrophication, acidification, ecotoxicity and human toxicity, land use

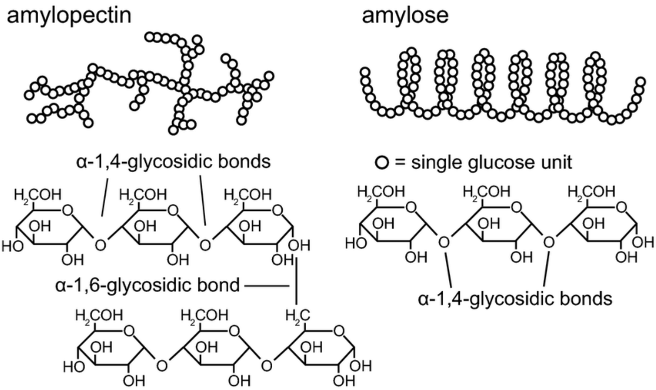
A. Vlasopoulos, J. Malinauskaite, A. Żabnieńska-Góra, H. Jouhara, Energy, 2023, Volume 277

Truth or false?



- Recyclables need to be washed and scrubbed, which wastes water
- The biodegradable plastics should be thrown to the same bin as the conventional plastics
- All biodegradable items are compostable
- All plastic items marked with the chasing recycling arrows are recyclable
- Biodegradable polymers degrade easily in the sea
- Recycling uses more energy/resources than it saves

Structure and properties: starch



- non-toxic, biodegradable, biocompatible
- poor mechanical properties, low impact resistance, water sensitivity, and brittleness properties

Willfahrt, A., Steiner, E., Hötzel, J. et al. Appl. Phys. A 125, 474 (2019)

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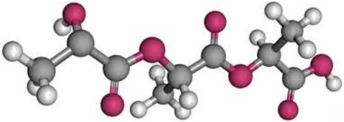
INNANOMAT MATERIALS FOR INNOVATION

Structure and properties: poly(lactic acid)

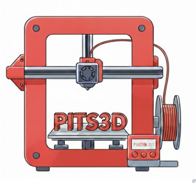


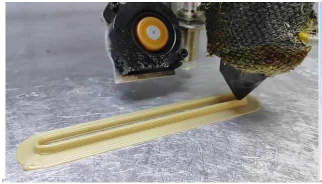
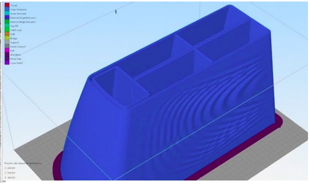




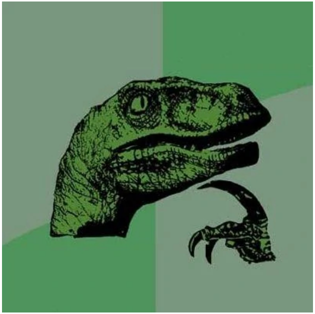
- easy to melt, good mechanical properties, non-toxic
- low heat resistance, biodegradable under certain conditions

Additive manufacturing



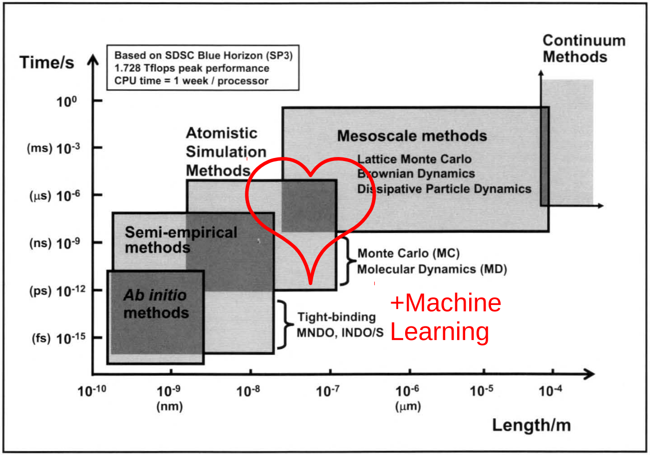



- layer-by-layer deposition of melted material
- fused deposition modeling, fused filament fabrication, stereolithography, selective laser sintering
- near-net-shape production
- recycled or bio-based feedstock
- rapid prototyping of missing pieces



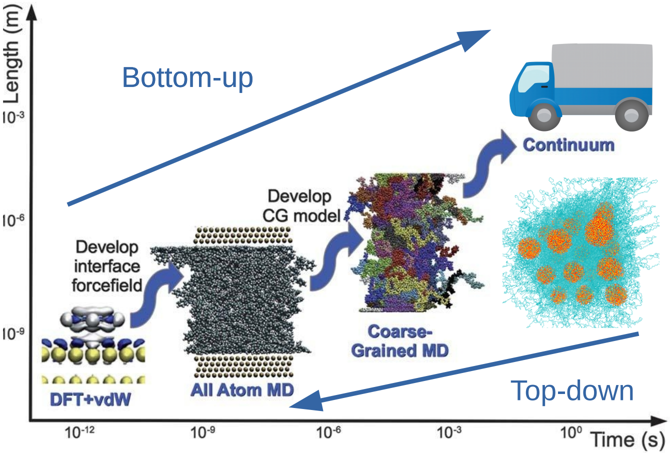
Identify the drawbacks of additive manufacturing.

Computational methods: time and length scales



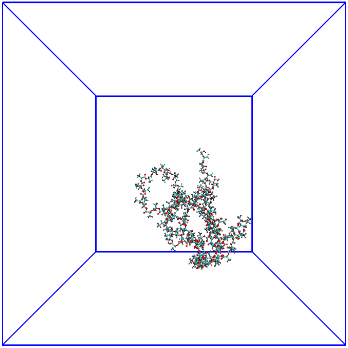
F.R. Hung, K.E. Gubbins, and S. Franzen, Chemical Engineering Education, Fall 2004

Bottom-up vs. Top-down



K. Johnston, V. Harmandaris, Soft Matter, 2013,9, 6696-6710

Classical Molecular Dynamics



Starter pack:

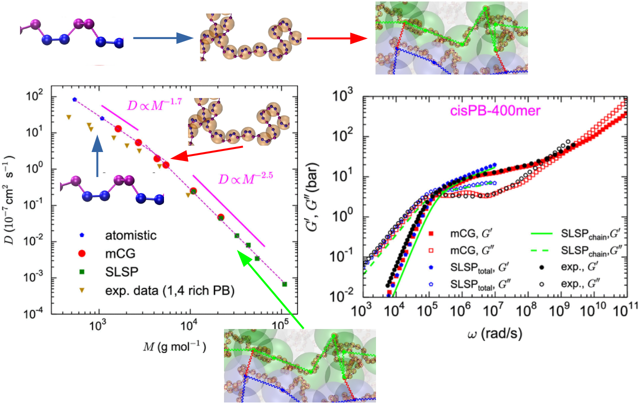
- initial state of the system under study: type of particles, mutual distances...
- interaction potential
- Newton's equations of motion

⇒ output: coordinates as a function of time (trajectory)

Bottom-up approach for tire industry

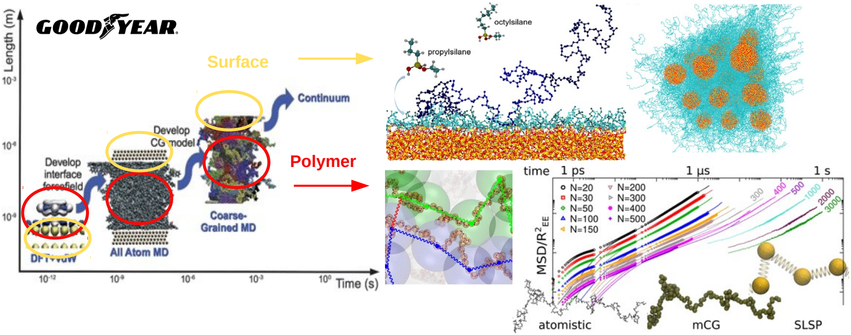
- polybutadiene of different composition
- systematic coarse graining

- ✔ full control of the compostion
- ✔ data base of properties



[1] A. F. Behbahani, L. Schneider, A. Rissanou, A. Chazirakis, P. Bačová, P. K. Jana, W. Li, M. Doxastakis, P. Polinska, C. Burkhart, M. Müller, V. Harmandaris, Macromolecules 2021 54 (6), 2740-2762

MD of hybrid systems

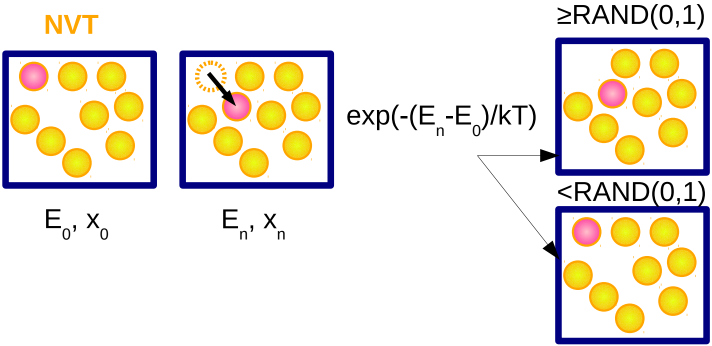


- adjusting the composition to get the best performance
- eco-friendly material design

[1] A. F. Behbahani, L. Schneider, A. Rissanou, A. Chazirakis, P. Bačová, P. K. Jana, W. Li, M. Doxastakis, P. Polinska, C. Burkhart, M. Müller, V. Harmandaris, Macromolecules 2021 54 (6), 2740-2762

Metropolis Monte Carlo

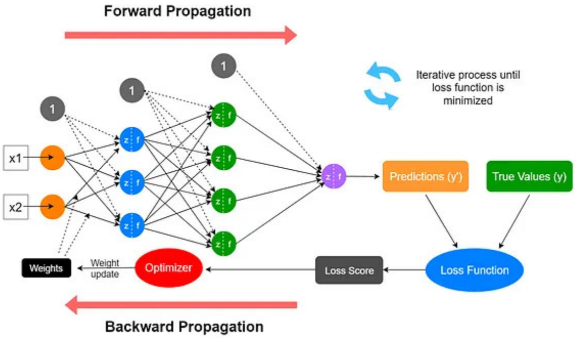
- instead of a system evolution according to the equations of motion, the particles move according to certain probability
- sampling according to the ensemble



Machine Learning

Neural Networks

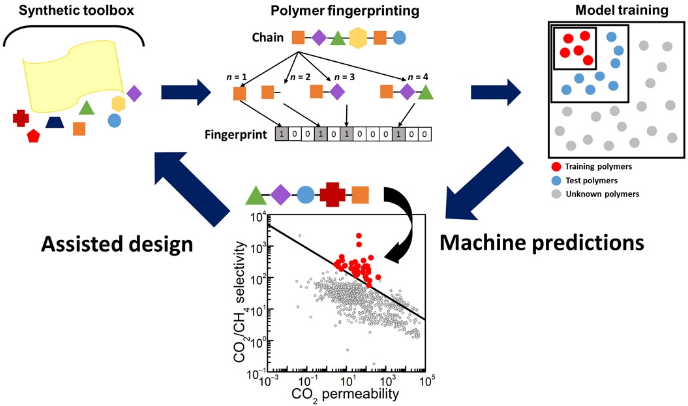
- computers using algorithms and statistical models to combine input to produce useful predictions on never-before-seen data



https://medium.com/data-science-365/overview-of-a-neural-networks-learning-process-61690a502fa

Neural networks: polymer membranes

- translate the polymeric structure of published data into a binary fingerprint



Barnett, J. W. et al. Sci. Adv. 2020, 6, 4301

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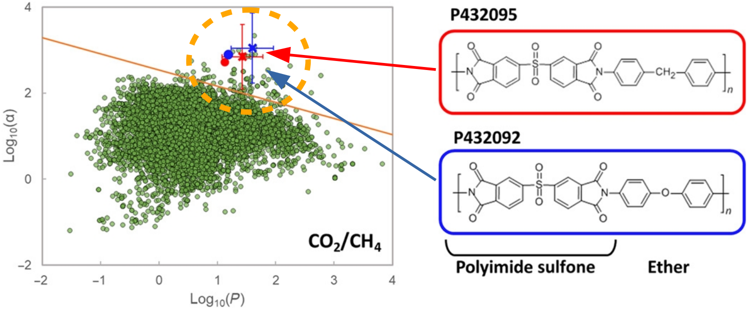
INNANOMAT MATERIALS FOR INNOVATION

Neural networks: polymer membranes

- algorithm capable of predicting permeability of materials not tested for this property before
- 2 materials synthetized, they outperformed the published data set



Thanks for making it till the end!
Keep calm and stay tuned!

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☞ https://polysim.eu/