Russian Supercomputing Days

KINTECH LABORATORY

ИНЭОС ВИНИТИ

September 23-24, 2024, Moscow

Using the MULTICOMP Package to Predict the Properties of Polymer-based Materials

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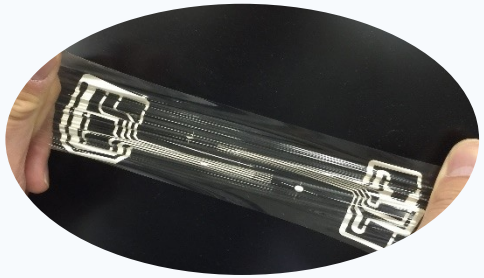
The work is performed on the basis of Kintech Lab Ltd.

polymer based materials: applications

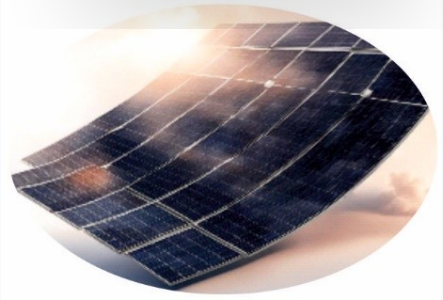


Flexible electronics

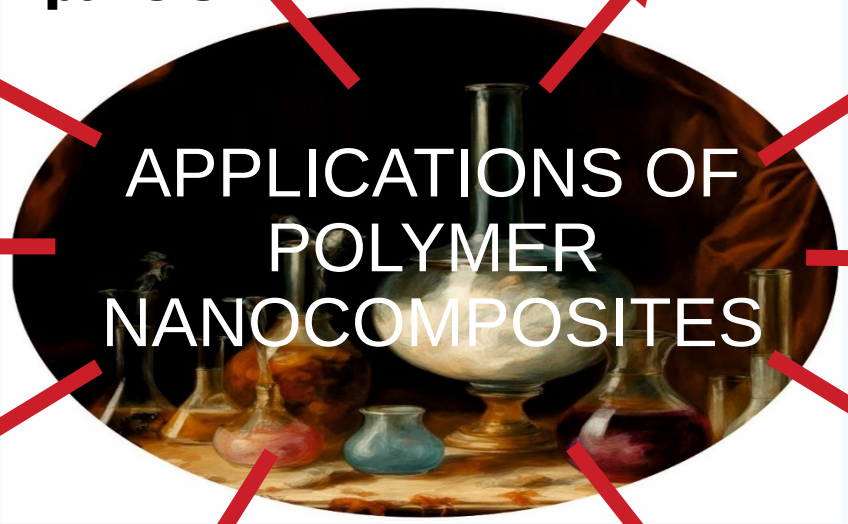
LCD panels

Medical

Gels



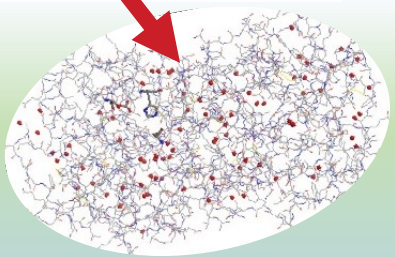
Organic photovoltaics



Glues / paints

hemical fibers

Transport



Syntetic catalysts

Packaging

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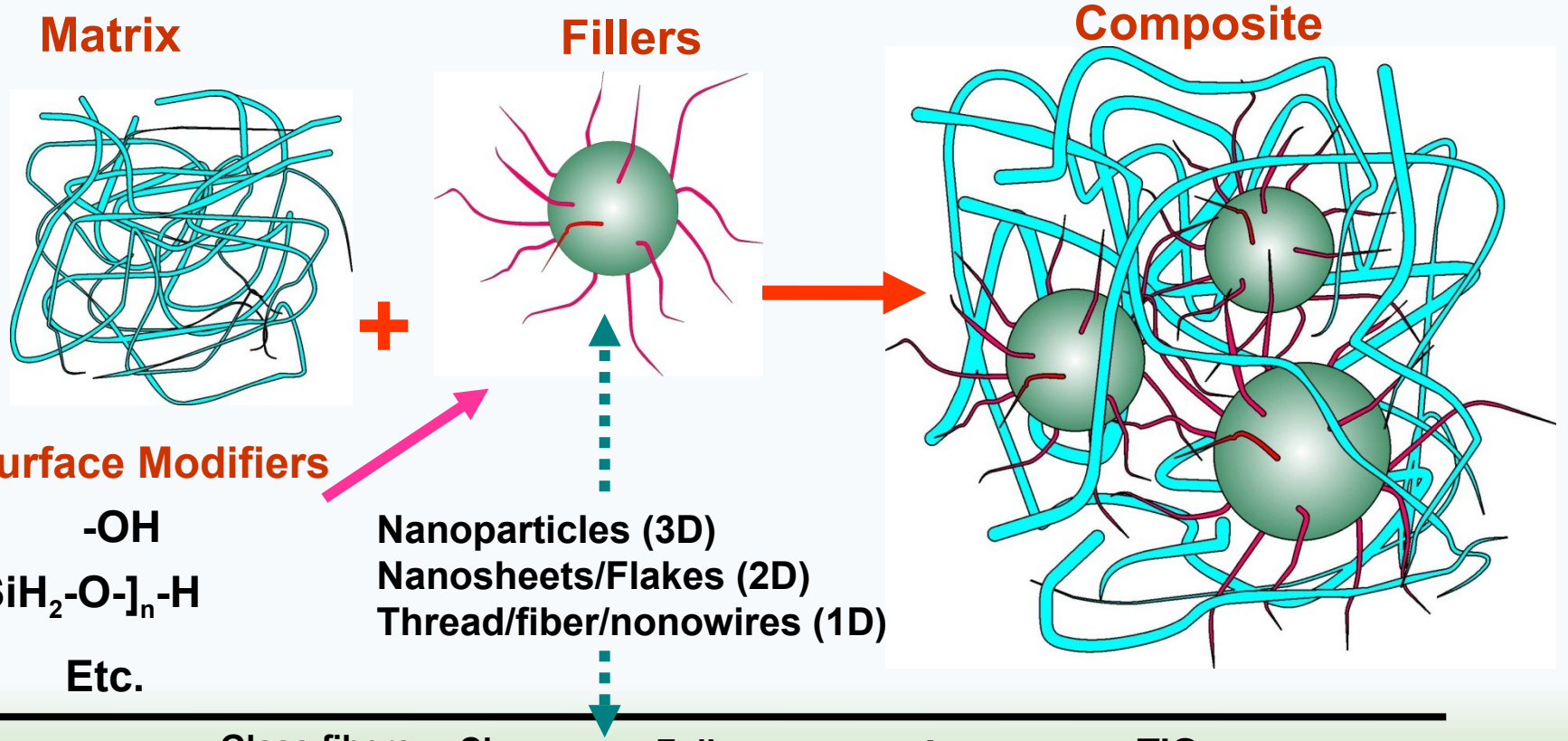
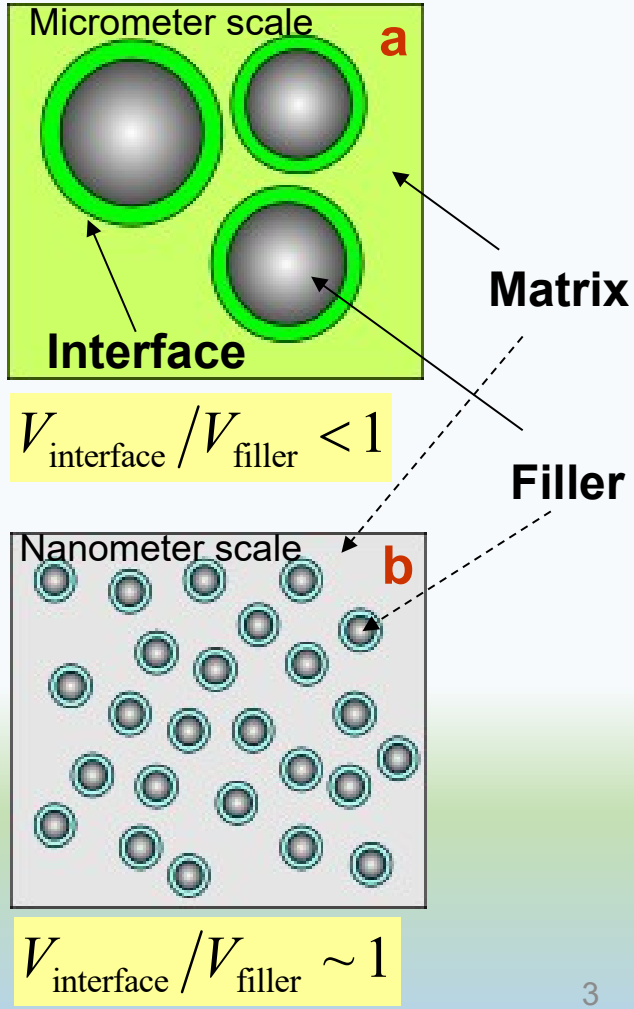
polymer nanocomposites

Combination of a polymer matrix and filler that have at least one dimension (i.e. length, width, or thickness) in the nanometer size range (1 nm = 10^{-9} m)

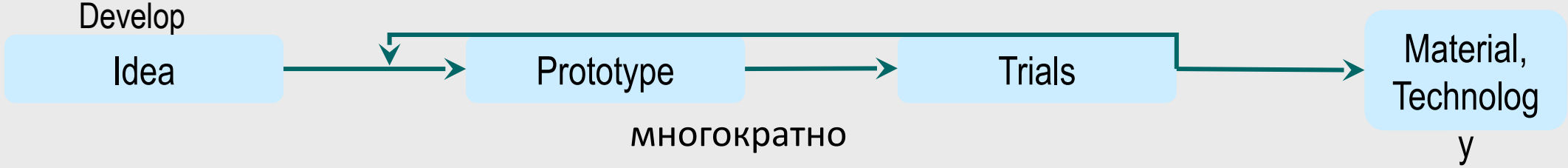
- **Composites** are materials consisting of two or more physically different phases, the combination of which leads to the emergence of new unique properties that differ from the characteristics of the original components.





polymer constructive materials: research & development

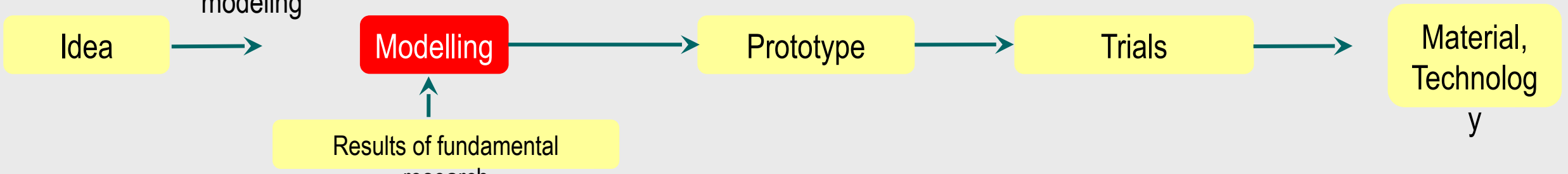
The Traditional Way to Create New Materials and Technologies: Empirical Try and Develop



✓ Expensive ✓ Lot of time ✓ Lack of direct connection with basic science

The role of modeling is reduced to describing data and extrapolating within model representations.

An integrated approach based on predictive modeling



✓ Reducing development costs and time ✓ Reducing risks

Predictive modeling based on detailed atomic-level understanding of structure and mechanism precedes prototyping

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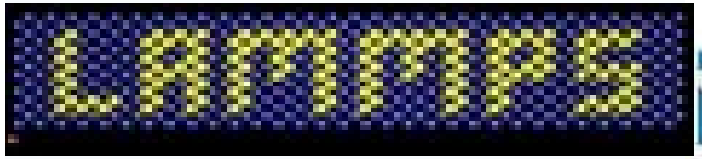
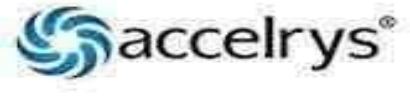
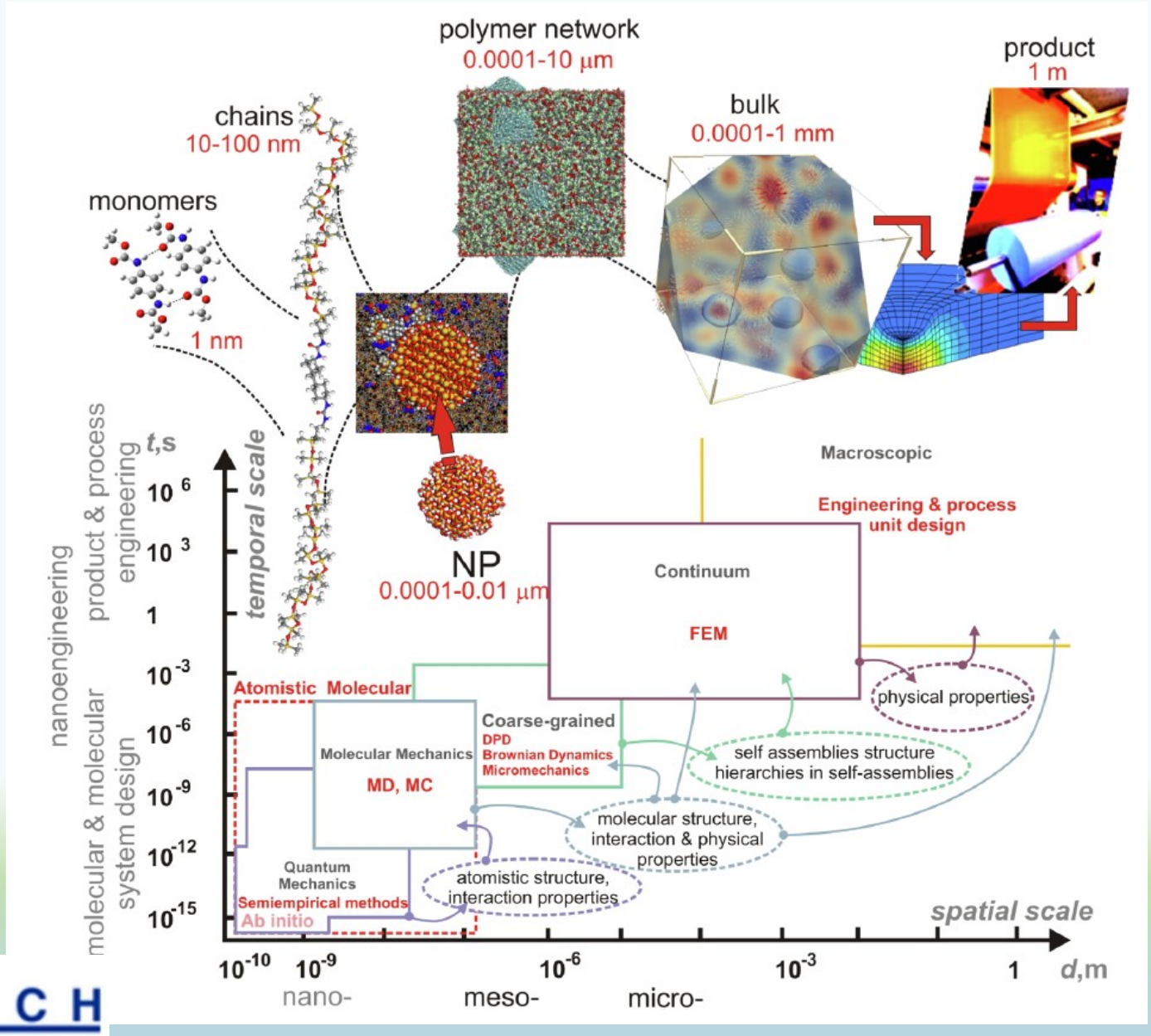
software for predictive modeling of polymeric material properties





polymer nanocomposites modeling: multiscale approach



In the case of nanocomposites, it is impossible within the framework of a one-level approach to combine high accuracy and large scale of consideration.

- **Atomistic level** - properties of nanosized filler and phase interaction
- **Mesoscal**e - the distribution of the filler in the matrix
- **Macro level** - effective material properties

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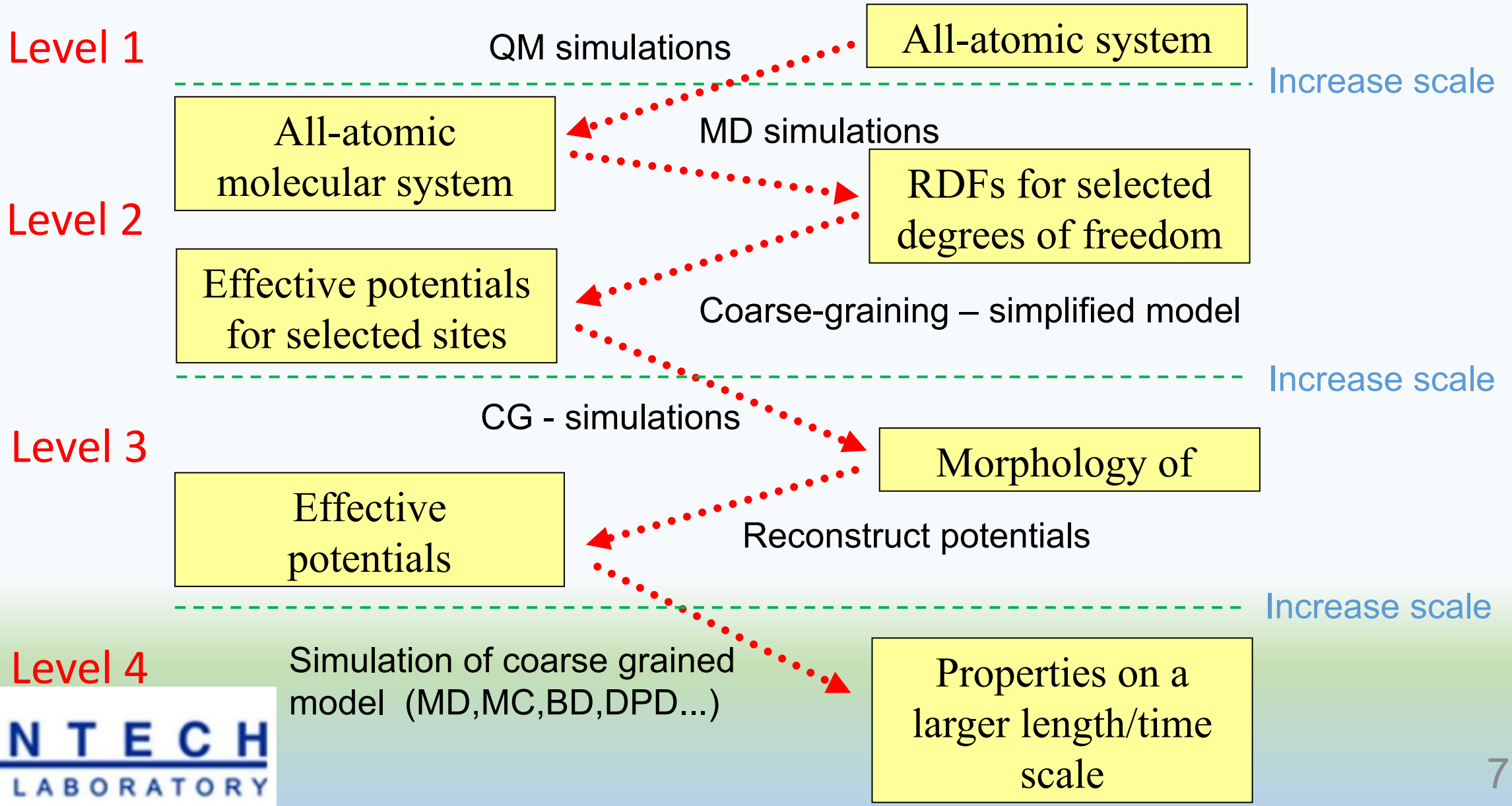
multi-scale modeling approach



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MULTICOMP software package for multiscale modeling of polymer-based materials

РОССИЙСКАЯ ФЕДЕРАЦИЯ

СВИДЕТЕЛЬСТВО

о государственной регистрации программы для ЭВМ

№ 2018615740

Multicomp

Правообладатель: *Общество с ограниченной ответственностью «Лаборатория Кинтех» (RU)*

Авторы: *см. на обороте*

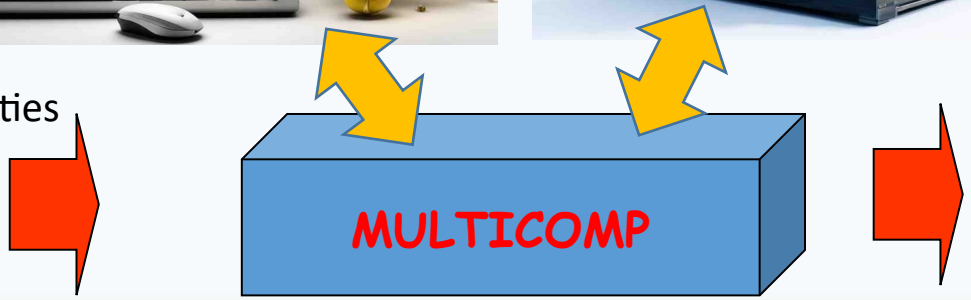
Заявка № 2018613030
Дата поступления 28 марта 2018 г.
Дата государственной регистрации
в Реестре программ для ЭВМ 15 мая 2018 г.

Руководитель Федеральной службы по интеллектуальной собственности Г.П. Ивлиев

Designed for high-throughput materials screening on supercomputers

input

- Chemical structure of components
- Geometry of nanoparticles and their properties
- Weight ratio of components
- Temperature, pressure and etc.



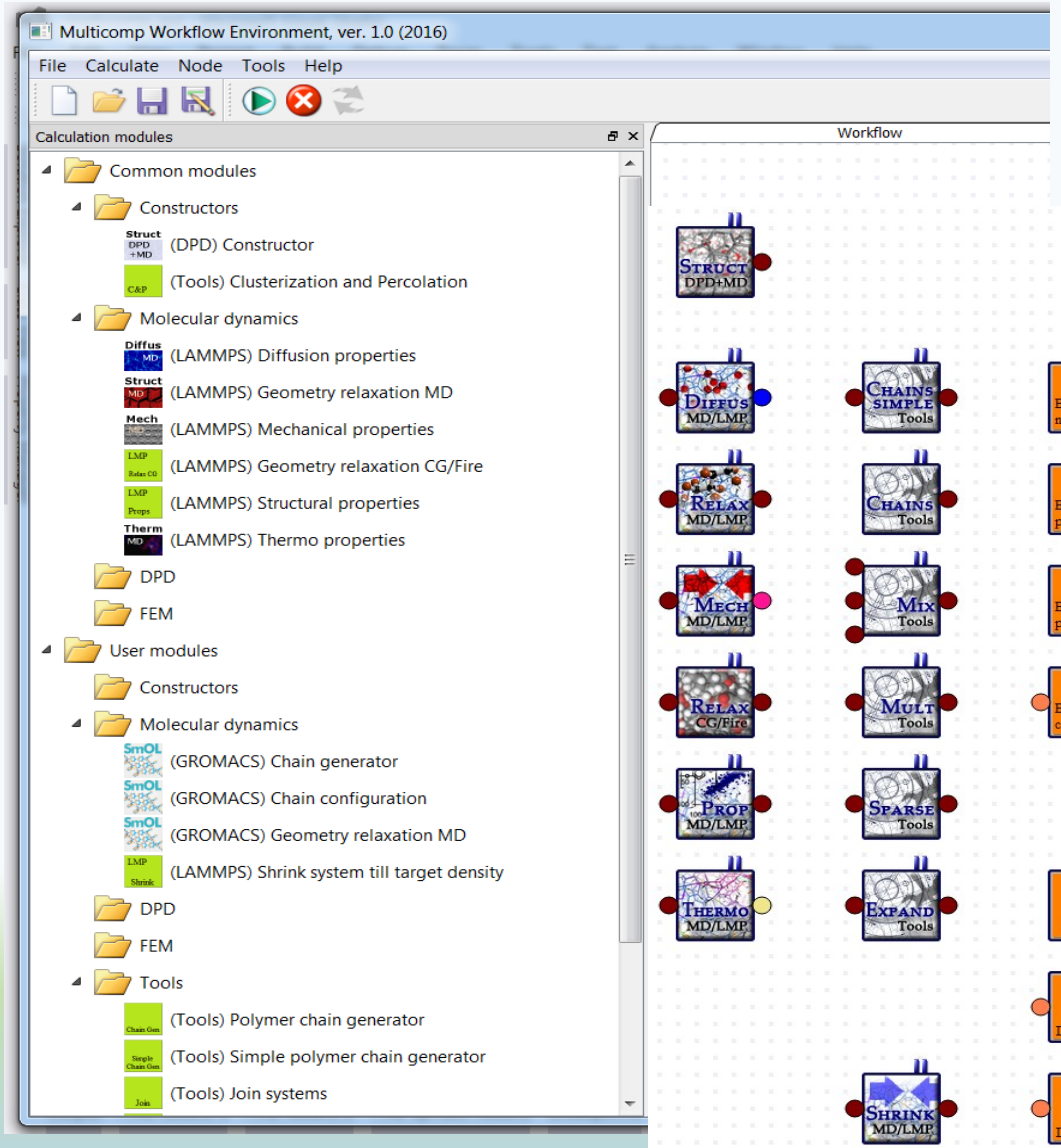
output

Physical properties of the material:

- structural
- mechanical
- thermophysical
- transport

M.A. Akhukov, V.A. Chorkov, A. A. Gavrilov, D.V. Guseva, P.G. Khalatur, A.R. Khokhlov, A.A. Kniznik, P.V. Komarov, M.V. Okun, B.V. Potapkin, V.Yu. Rudyak, D.B. Shirabaykin, A.S. Skomorokhov, S.V. Trepalin, **MULTICOMP package for multilevel simulation of polymer nanocomposites**,
Computational Materials Science, V. 216, 2023, 111832, **https://doi.org/10.1016/j.commatsci.2022.111832**.

modules kit



constructors

Nano/Meso tube Generator

Atomistic Constructor (K23)

Linear Meso-polymer Generator and Mixer

service tools

Simple Polymer Chain Generator

Polymer Chain Generator

Multiply System by copying

Expand System by translation

Join Systems.

Sparse System into Separate Molecules

Mix Systems

Select and Split

simulations tools

Geometry relaxation CG/Fire

Geometry relaxation MD

Shrink system till target density

Meso Structure Relaxation MD

Meso Structure Relaxation CG

calculation and analysis of properties_

Mechanical properties

Thermo properties

Diffusion properties

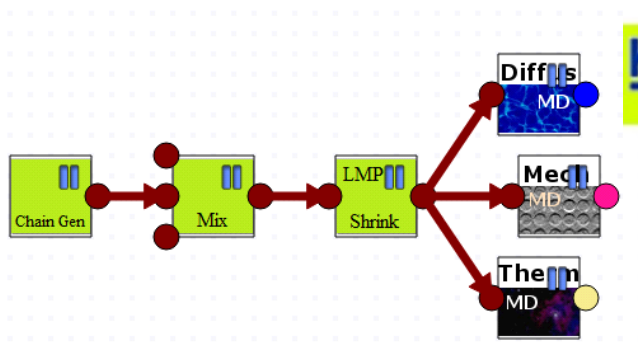
Structural properties

(density, RDF, XRD, SAED, porosity)

Clusterization

Percolation

Atomic Percolation



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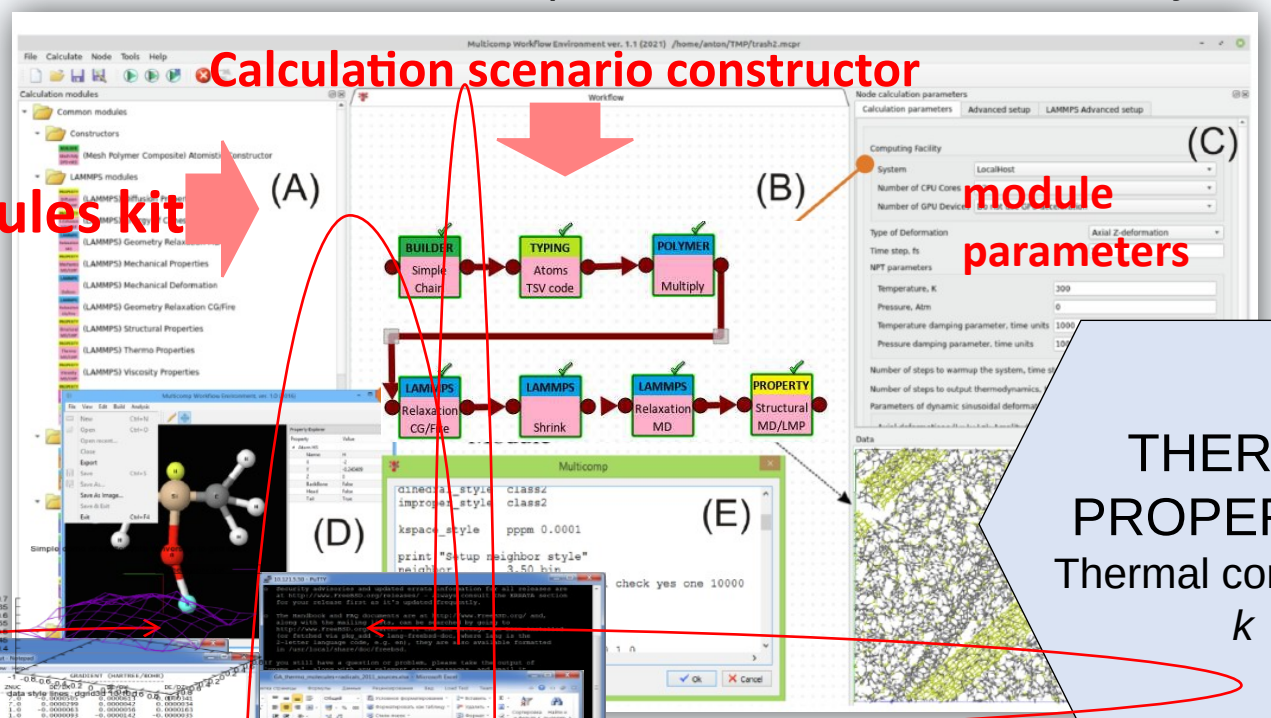
Graphical User Interface: scientific workflow approach

The modeling process is divided into separate modules at a fixed level of the spatial and time scale hierarchy



STRUCTURAL PROPERTIES
Porosity, radial distribution function
XRD / ED spectra

MECHANICAL PROPERTIES
Young moduli *E*
Poisson ratios *σ*
Bulk moduli *K*/*G*

BARRIER PROPERTIES
Diffusion D Solubility S
Permeability P

THERMO PROPERTIES
Thermal conductivity *k*

VISCOSITY PROPERTIES
Kinematic/dynamic viscosity *v*/*μ*

CHEMICAL COMPOSITION

MATERIAL MODEL

PHYSICAL PROPERTIES

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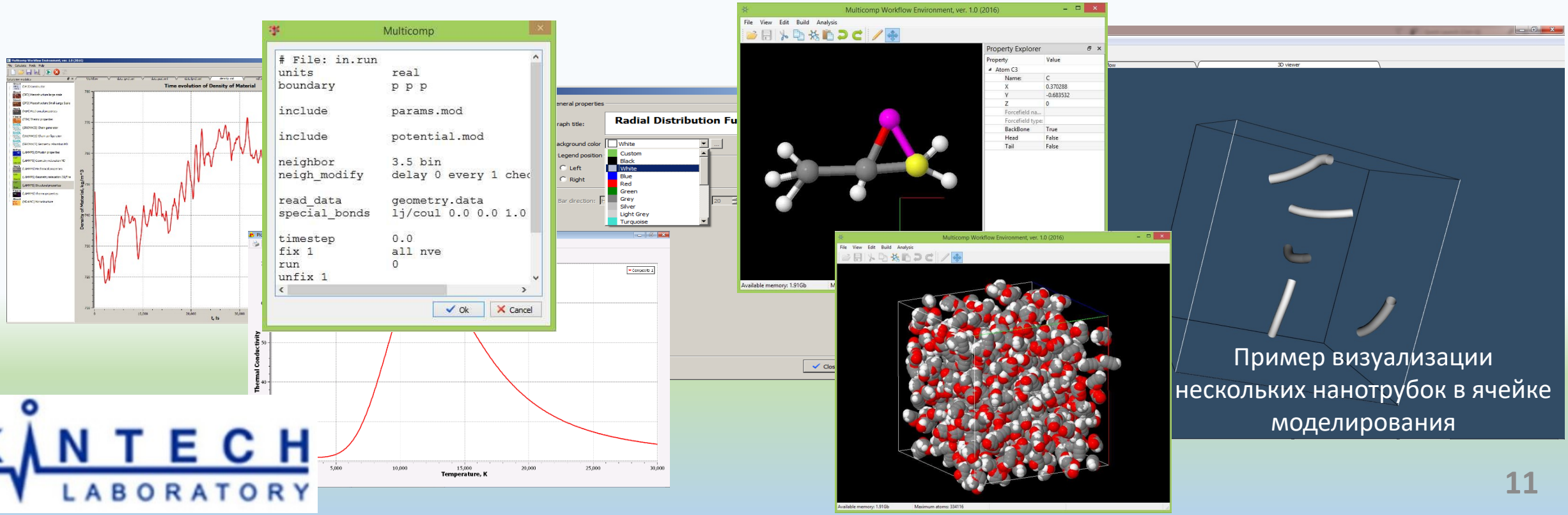
visualization

- The results are displayed using an interactive 1D / 2D / 3D visualization module consisting of 2 blocks: 1D visualization and 2D / 3D visualization.
- Block 1D visualization consists of an embedded window for displaying functional dependencies, a separate form containing a display window and a toolbar, a window for setting display parameters and auxiliary windows.
- The 2D / 3D visualization block consists of a built-in window for displaying 2D / 3D objects and grids and a separate form containing the display window, the main menu and the toolbar.

embeddable window for displaying functional dependencies

embedded 2D / 3D object and mesh display window

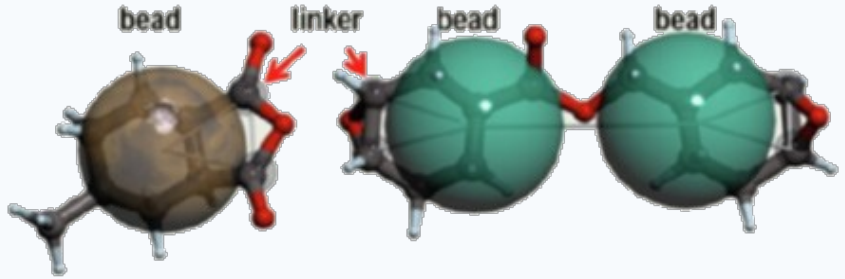


cross-linked matrices and composites constructors

Polymerization at mesoscale (Network building procedure)

To simulate the network formation process, we used a model of chemical reaction systems based on the DPD framework and our concept of *composite CG/DPD particles* which are composed of two different types of CG sites: *non-reactive beads* and *reactive linkers*.

Beads are normal CG particles - they participate in all site–site interactions, while linkers are semi-virtual sites - they participate in intramolecular interactions only (namely, in bond stretching and bond angle bending interactions) but can form covalent bonds; that is, they can react.



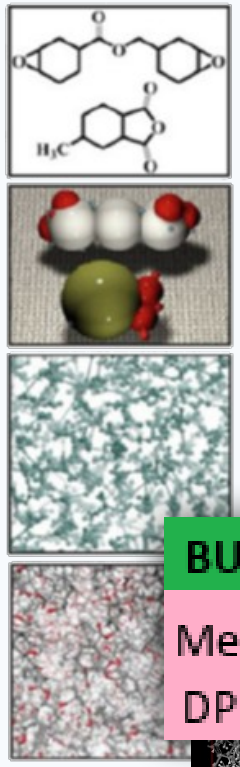
The positions of beads and the topology of inter-bead connections are determined with the Neural-Gas-based algorithm.

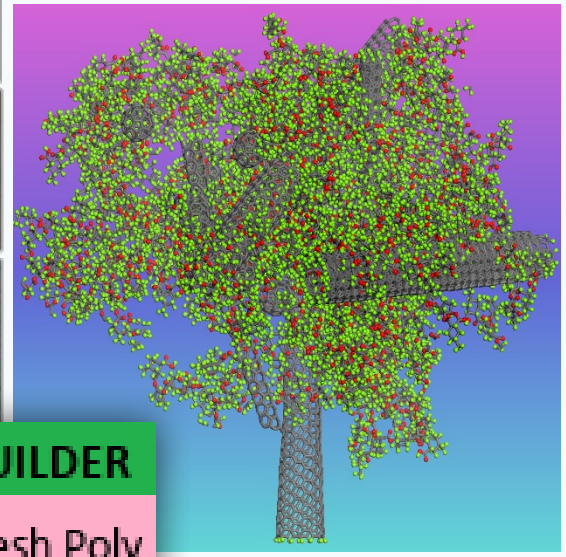
MOLECULAR EDITOR

CONSTRUCTION
NG-based coarse-graining

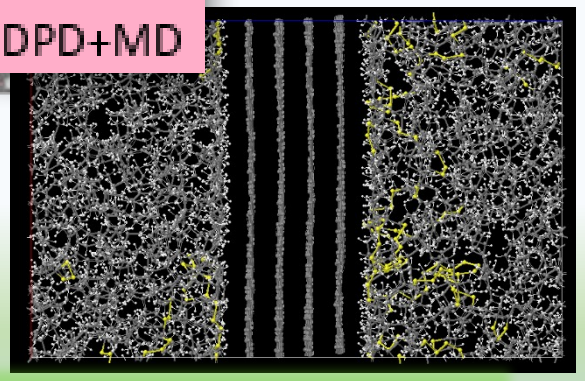
POLYMERIZATION
MSC-based reactive DPD

RECONSTRUCTION
reverse mapping CG to atomistic structure





BUILDER
Mesh Poly
DPD+MD



Tasks that can be effectively solved using the Mesh Poly DPD+MD module:

- ✓ Crosslinked polymer blends
- ✓ Polymer composites with a cross-linked matrix (including on a substrate)

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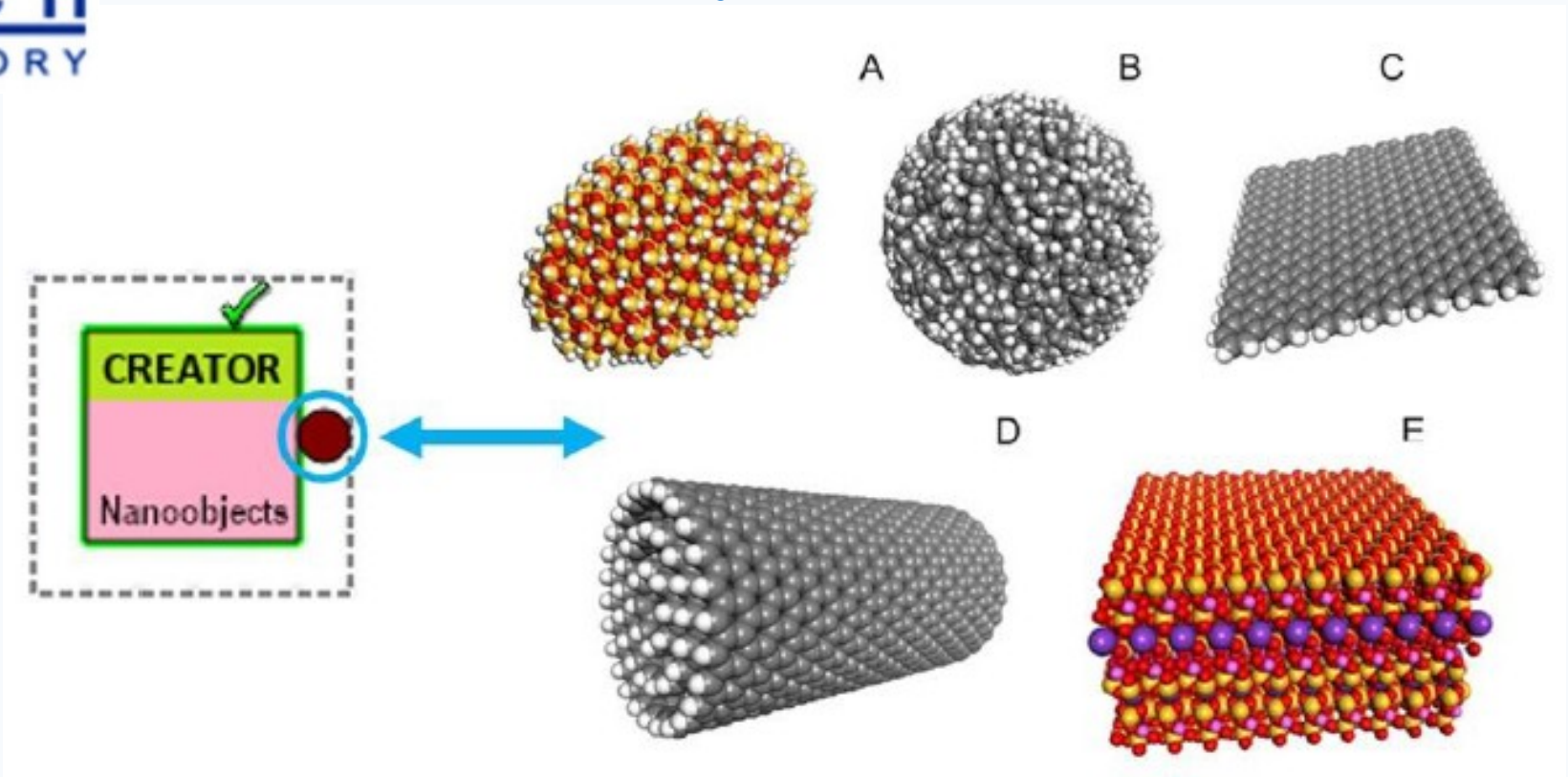
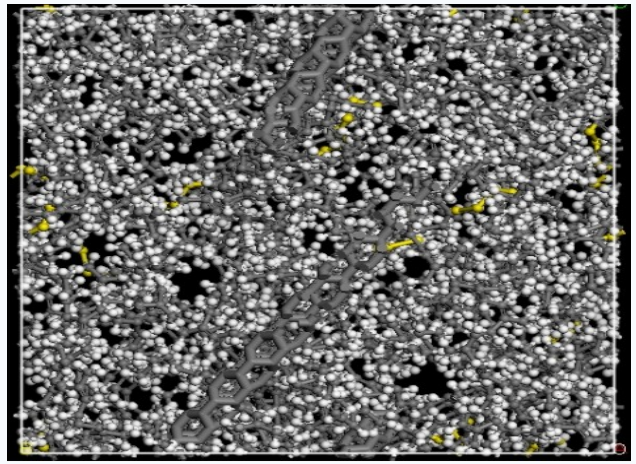
✓ THE ABILITY TO QUICKLY AND EASILY CONSTRUCT A VARIETY OF CROSS-LINKED MATRICES AND NANOCOMPOSITES

NANOOBJECTS: module for creating nanoparticles

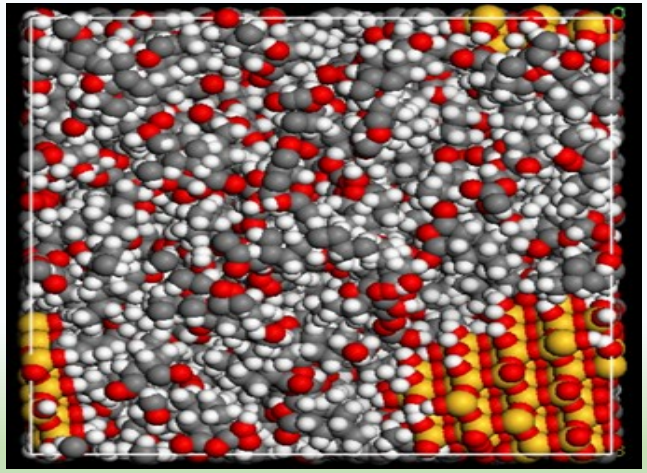


Examples of nanostructures created by Nanoobjects: A) ellipsoidal silica nanoparticles with axial lengths of 30Å, 30Å, 50Å; B) spherical carbon black nanoparticles with a diameter of 40Å; C) rectangular graphene nanoparticles with a size of 30Å×30Å; D) three-walled carbon nanotube with a length of 41Å and an outer diameter of 21Å; E) flat muscovite surface with dimensions of 52Å×54Å×41Å.

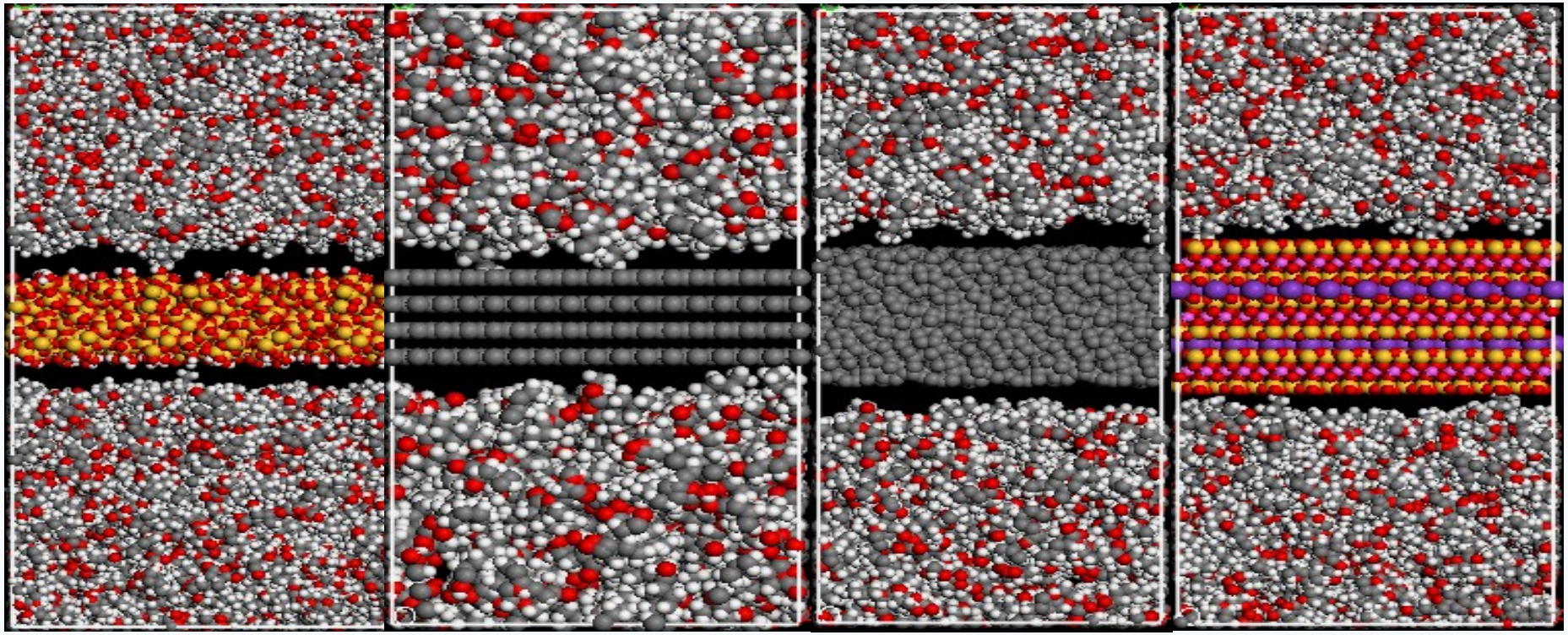
examples of polymer nanocomposites considered



elastomer + SWNT



epoxy resin + SiO2



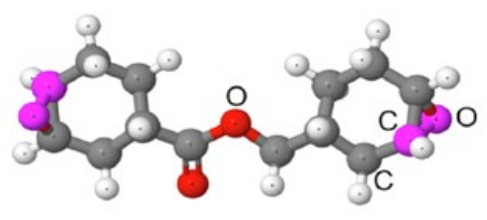
Epoxy resin on various substrates

calculation of the mechanical properties of crosslinked epoxy matrices

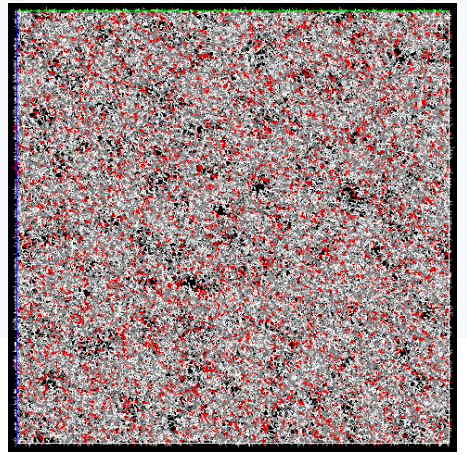
For crosslinked epoxy matrices, the literature shows a change in the modulus of elasticity depending on the degree of crosslinking .

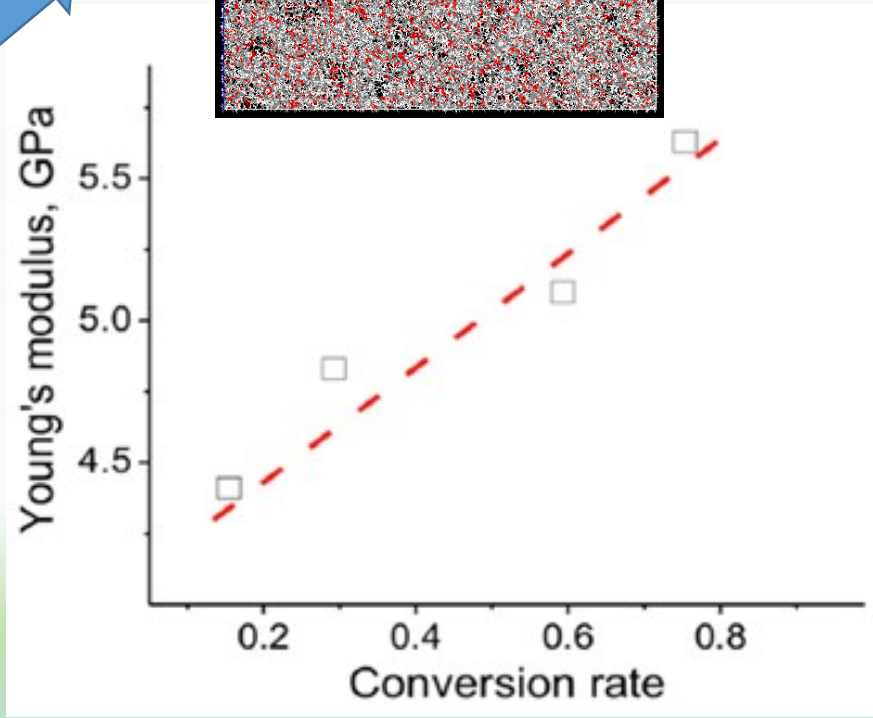
The morphology of polymer networks can be studied at the atomistic scale .

Epoxy monomer



Hardener





Calculation script

Using the constructor, it is convenient to study the dependence of physical properties on the degree of matrix crosslinking

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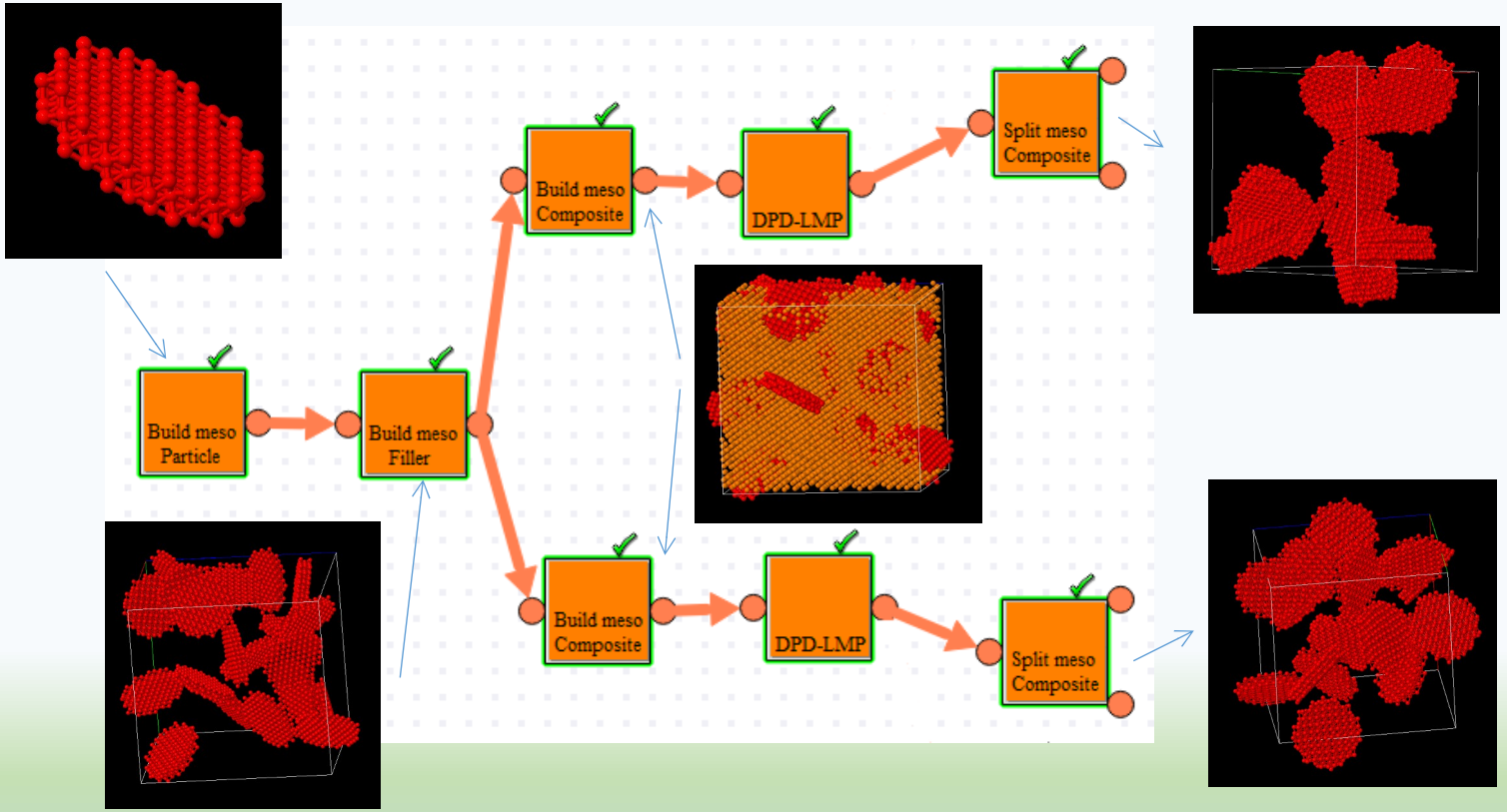
1 - Li C., Strachan A. Molecular dynamics predictions of thermal and mechanical properties of thermoset polymer EPON862/DETDA //Polymer. – 2011. – Т. 52. – №. 13. – С. 2920-2928.
2 - Komarov P. V. et al. Multiscale Simulations Approach: Crosslinked Polymer Matrices //Supercomputing Frontiers and Innovations. – 2018. – Т. 5. – №. 3. – С. 55-59.

relaxation of structures and distribution of filler

Different parameters of the interaction between the matrix and the filler lead to different distribution of the filler in the matrix.



Filler particles are repelled weaker from each other than from the matrix:
Filler aggregation

Filler particles are repelled more strongly from each other than from the matrix.
Homogeneous distribution

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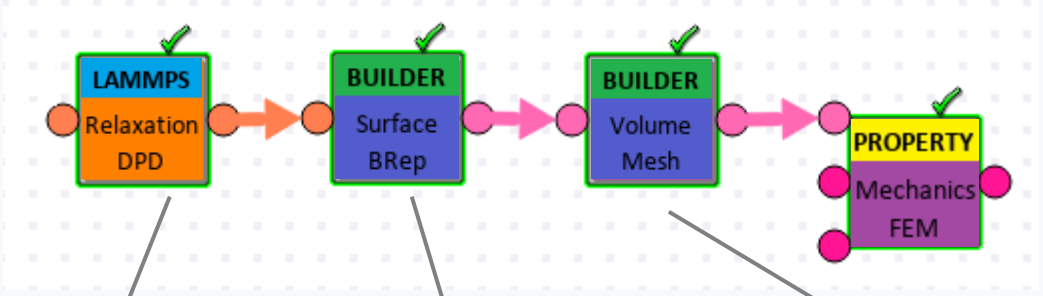
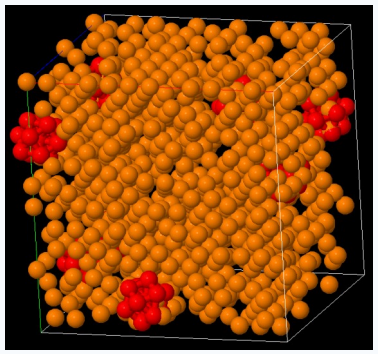
It is possible to predict the distribution of the filler depending on its interaction with the matrix

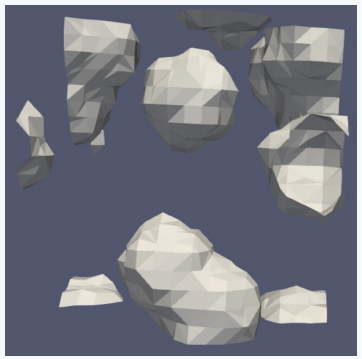
transition to properties calculation at the macro level

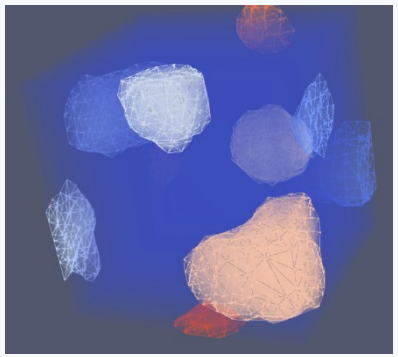
Implemented universal procedure for direct conversion from the meso level to the macro level (regardless of the shape, location and concentration of the filler) before calculation of the effective properties of the material using the Marching Cubes method.

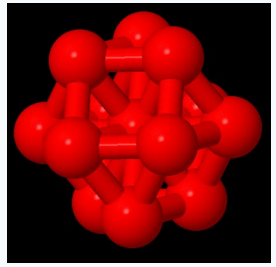


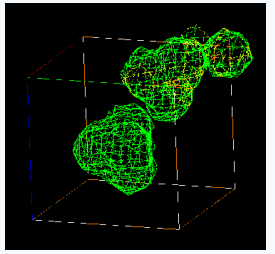
Composite
Elastic tensor
calculation

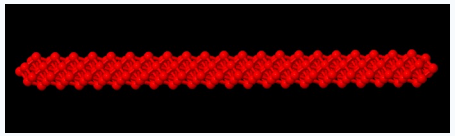


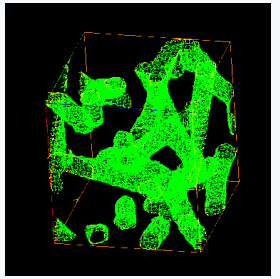


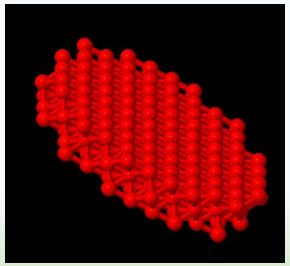


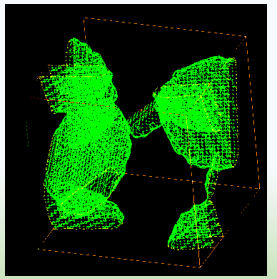












At the macro level, engineering properties (mechanical properties, thermal conductivity) are calculated using the finite element method (FEM).

TRANSITION PROCEDURE TO THE MACRO LEVEL IS FULLY AUTOMATED AND UNIVERSAL FOR ANY FORM OF FILLER

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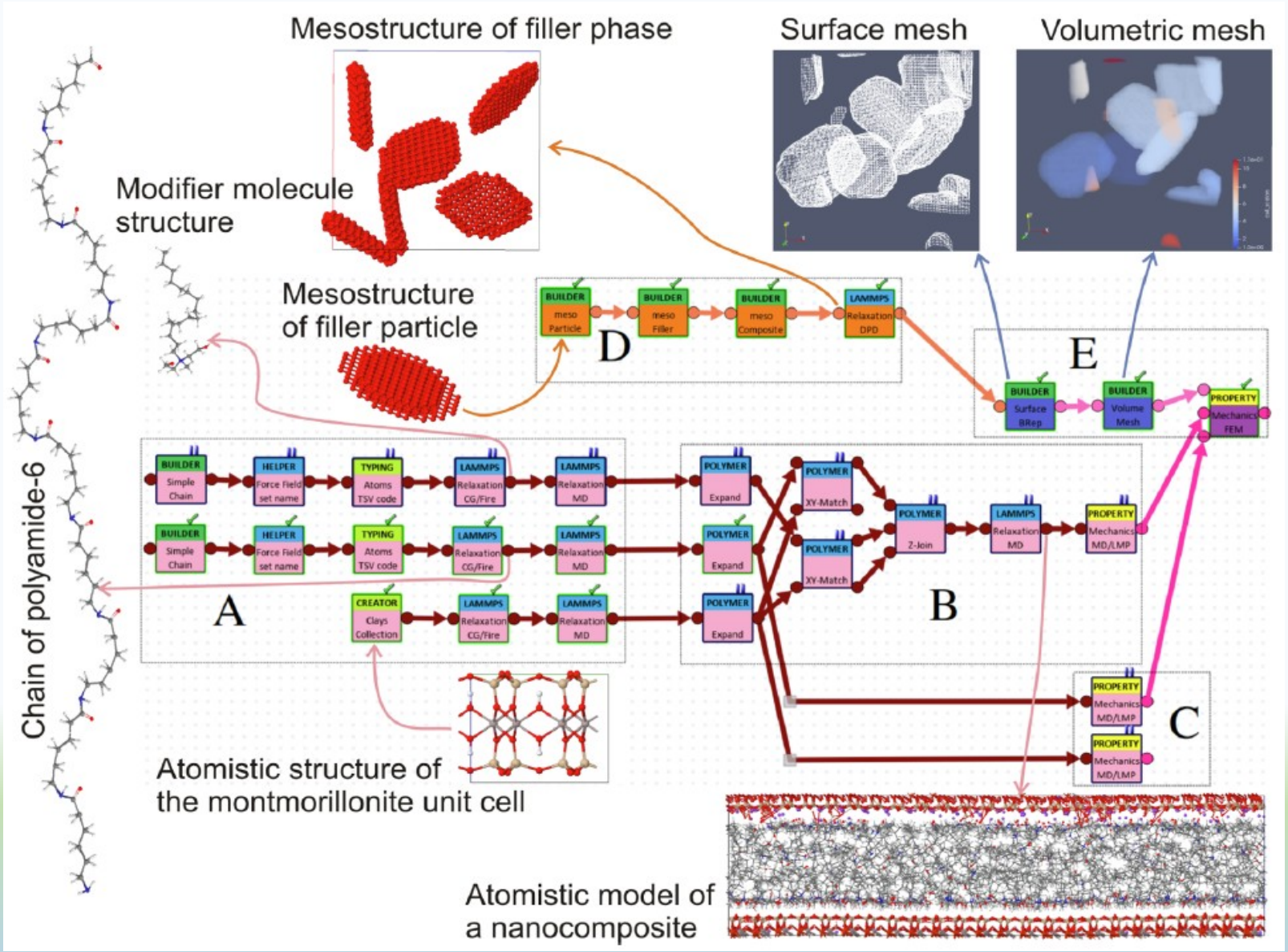
Akhukov, M. A et al. // Computational Materials Science 2023 , 216, 111832

case study: multiscale calculation of macroscopic elastic modulus of the PA6-MMT nanocomposite



- The mechanical properties of the composite are different from the composition of the properties of the components due to the formation of a transition layer, whose elastic modulus is twice the elastic modulus of the matrix
- The increase in the elastic modulus of the material was 18% when filled by 1 wt.%. With the best structural parameters (experiment*), it is possible to increase the elastic modulus by up to two times
- The method is universal and allows you to calculate the properties of different structures: for an isotropic distribution of filler (1 and 100) module 4

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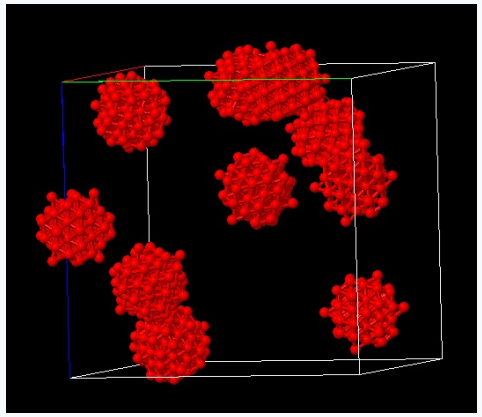
* - Kojima Y., Usuki A., Kawasumi M. et al. // J. Appl. Polym. Sci. 1993. V. 49. № 7. P. 1259

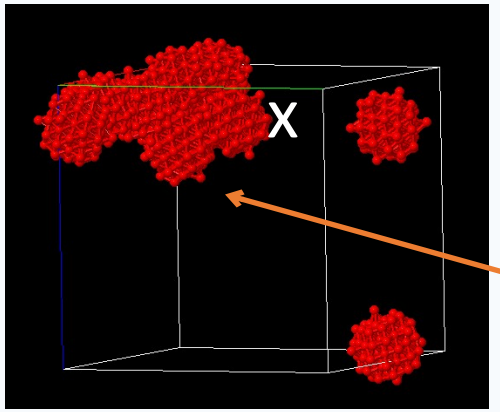
Akhukov, M. A et al. // Computational Materials Science 2023 , 216, 111832

calculation of the mechanical properties of a composite filled with spherical particles

Different distributions of the filler lead to different values of the elastic moduli at the same volumetric concentration of the filler, as well as anisotropy of properties. With percolation, the rigidity of the system in this direction increases significantly.

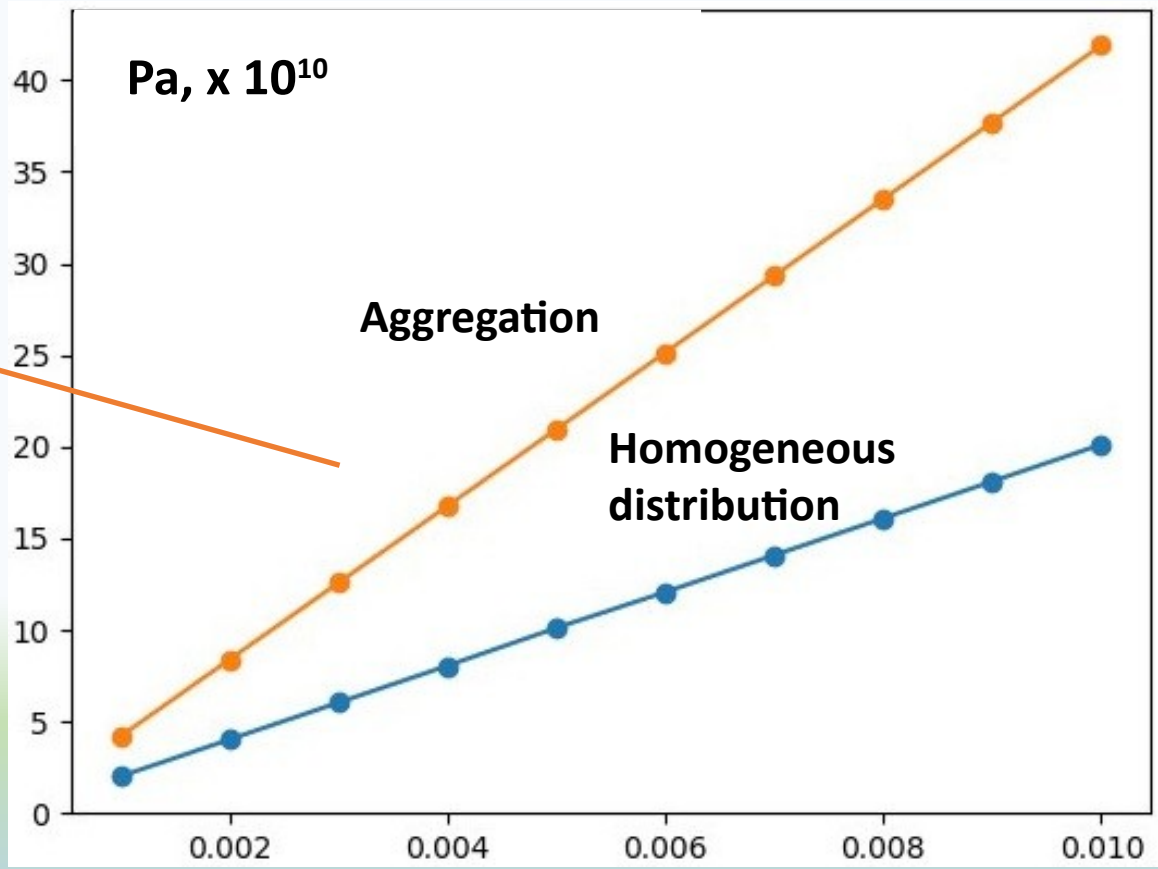


Aggregation
E = 4.2 GPa



Homogeneous distribution
(percolation along - x)
E_x =11 GPa

Dependence of stresses on deformation (along x, direction of percolation in one of the structures)



Data transfer for structure conversion and calculation of effective properties at the macro level are carried out automatically.

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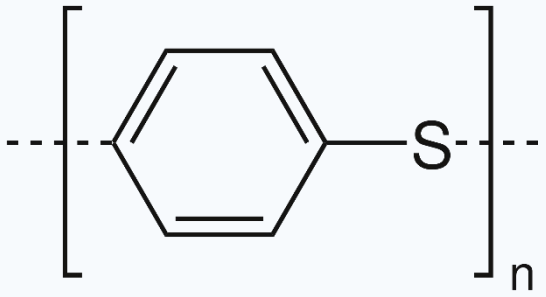
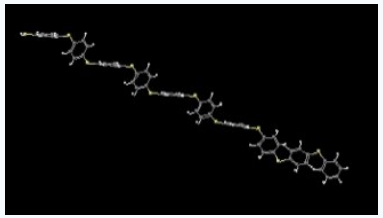
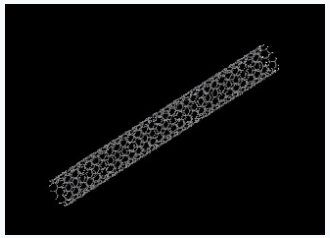
calculation of thermoconductivity of polyphenylene sulfide / CNT composite



Polyphenylene sulfide





Carbon nanotube

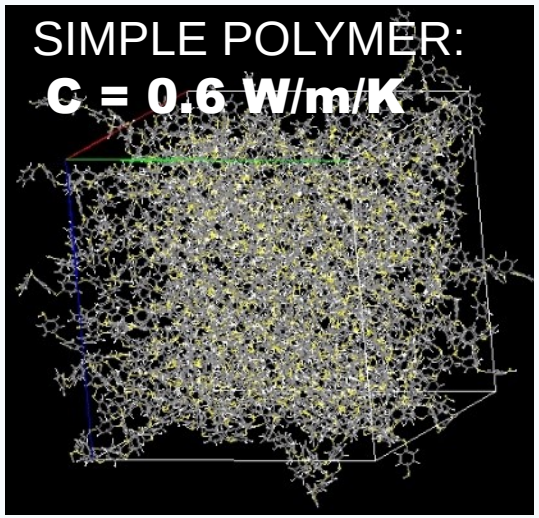
PROPERTY

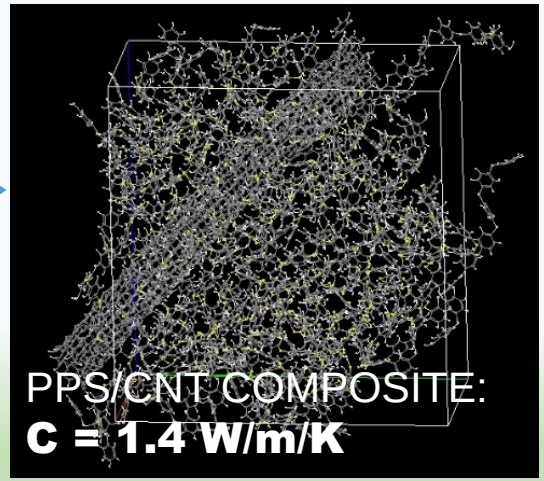
Thermo

MD/LMP

POLYMER

Mix





- When a polymer is filled with nanotubes, the thermal conductivity coefficient increases threefold
- Anisotropy of the thermal conductivity coefficient is observed: in the direction coinciding with the orientation of the nanotubes, it is significantly higher
- The change in the thermal conductivity coefficient of polymer matrices when they are filled with nanotubes[1] is widely described in the literature, where theoretical studies with similar results are presented.
- Changes in mechanical pr[illegible]ved

✓ POLYMER NANOCOMPOSITE CONSTRUCTOR THAT ALLOWS TO BUILD AND PARAMETERIZE AN ATOMISTIC STRUCTURE

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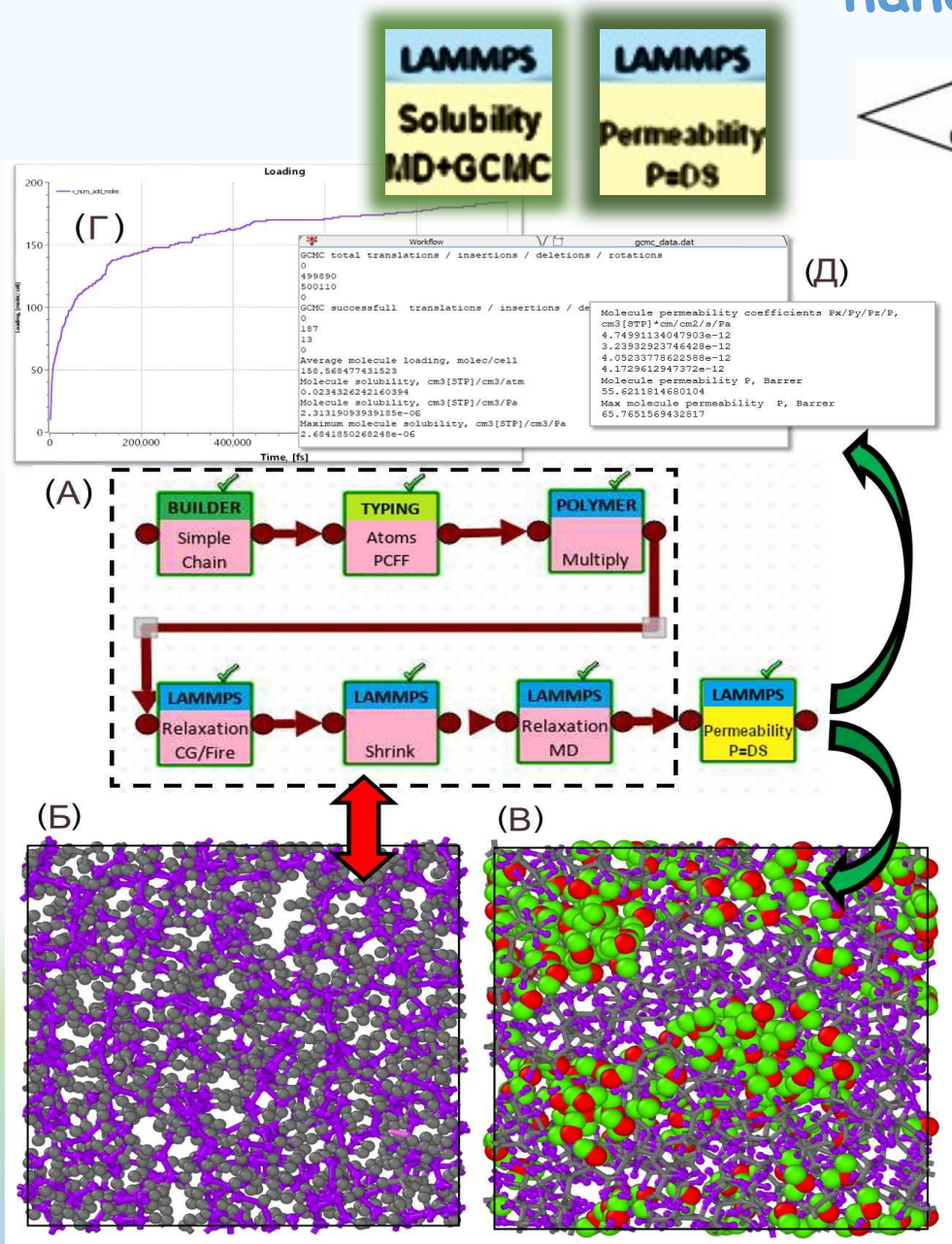
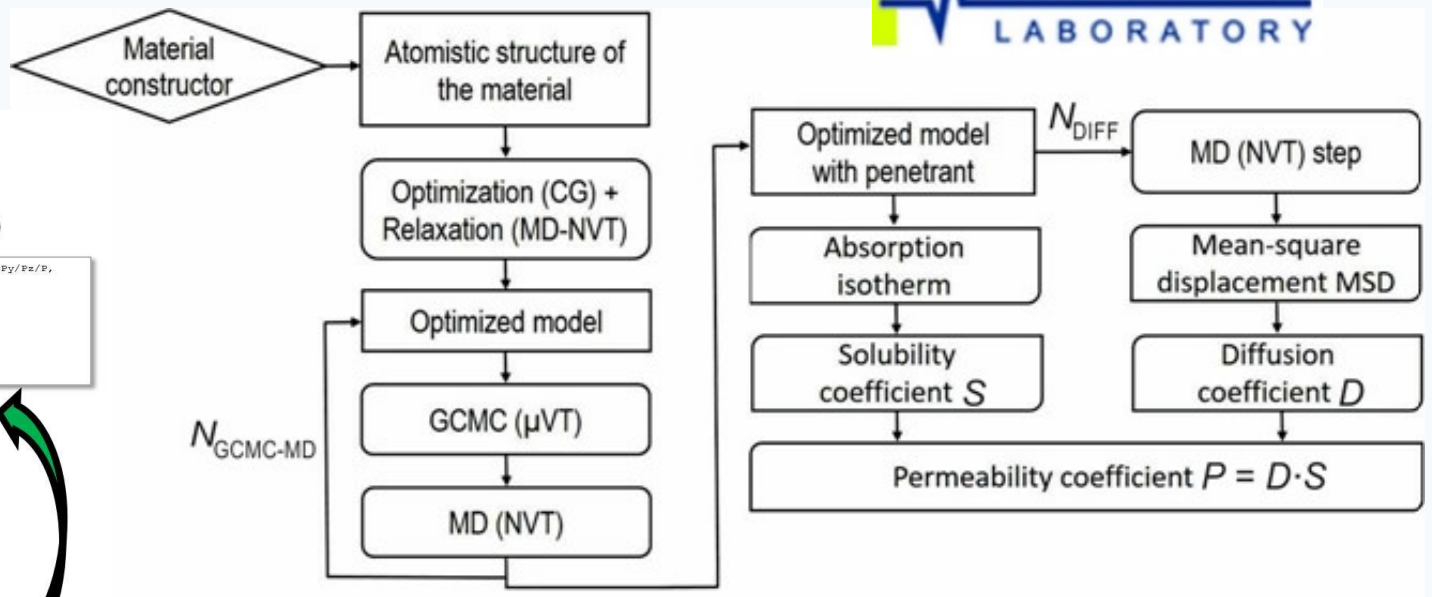
Naffakh M. et al. //Journal of Materials Chemistry. – 2012. – Т. 22. – №. 4. – С. 1418-1425.

case study: gas barrier properties of multilayer polymer-clay nanocomposite films

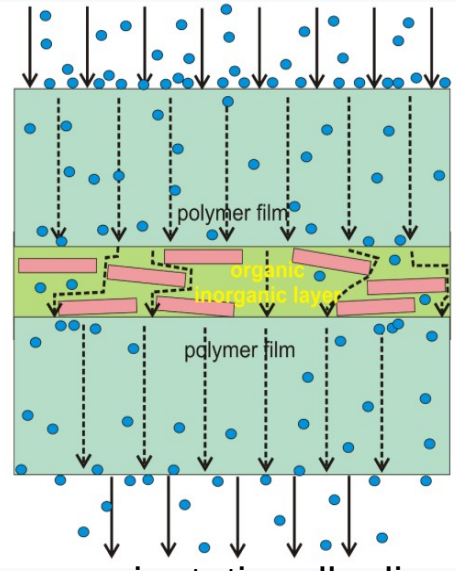




Material	$P(O_2)$ (Barrer)			$P(H_2O)$ (Barrer)		
	MD-GCMC Simulations	Bicerano Model	Experiment [NIMS]	MD-GCMC Simulations	Askadskii Model	Experiment [NIMS]
PET	0.01–0.02	0.04	0.013–5	1–2	87	100–1300
PE	0.2–0.6	4.47	0.04–5	2–12	60	20–75
PVDF	0.07–0.2	8.91	0.02–1.8	8–30	193	–
PTFE	17–22	7.65	2.5–6	10–50	328	3–8

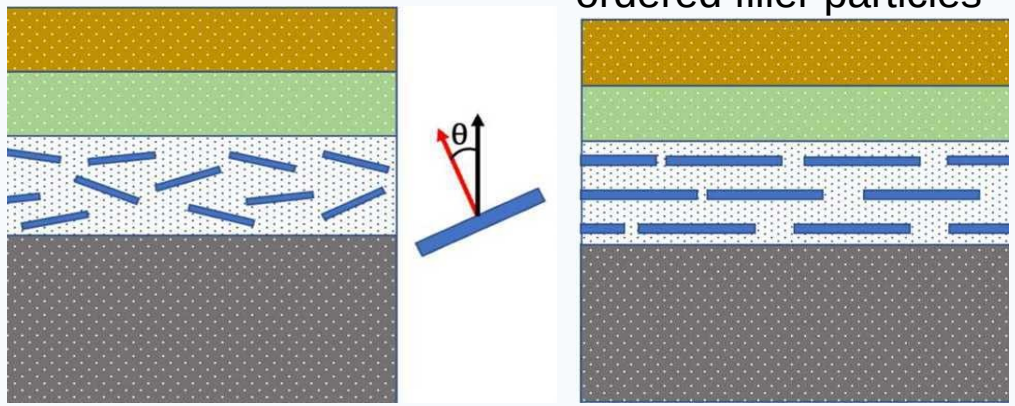
Knizhnik, A. A. et al // Minerals 2023, 13, 1151.

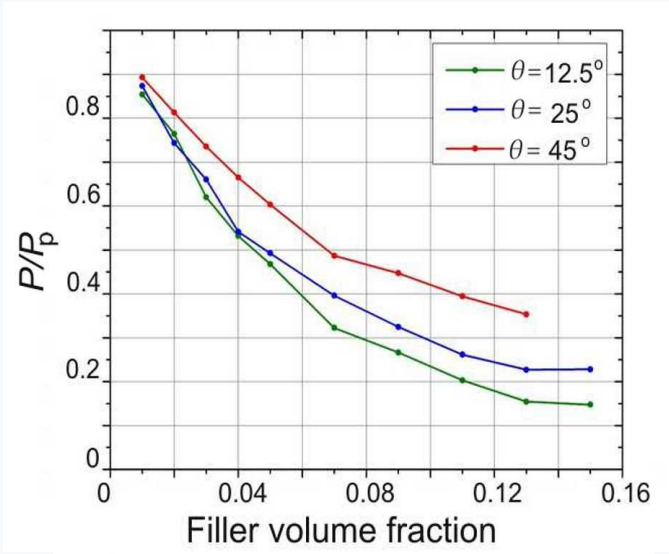
gas barrier properties of multilayer polymer–clay nanocomposite films - continuous model

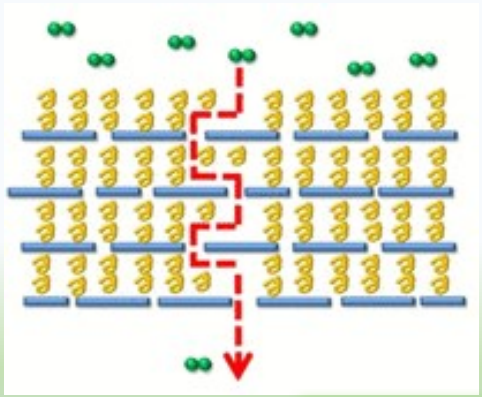


orientationally disordered filler particles

laminate with orientationally ordered filler particles

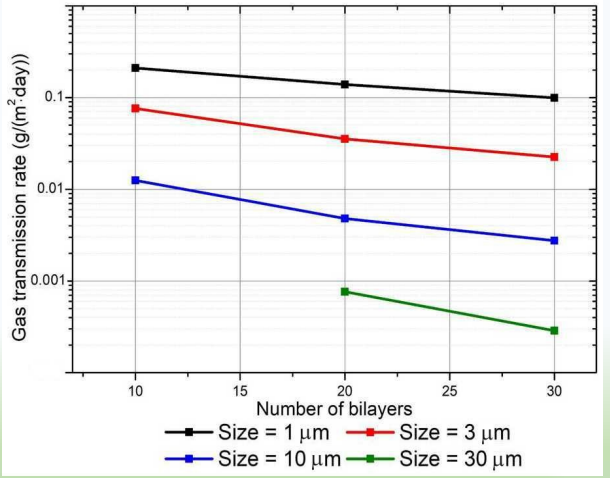






The model gives the diffusion time $\mathbf{t_{diff}}$ of the molecule throughout the multilayer coating (averaged over the number of attempts for a set of molecules). By comparing $\mathbf{<t_{diff}>}$ in a multilayer system with inorganic fillers and without them, the change in the permeability of the coating:

$$\frac{\quad}{\quad} = \frac{\quad}{\quad}, \qquad = \frac{1}{\sum}$$



✓ REDUCTION IN PERMEABILITY FROM THE ADDITION OF CLAY FILLERS TO THE POLYMERS IS OBTAINED WHEN USING MINERALS WITH FILLER PARTICLES WITH HIGH ASPECT RATIOS

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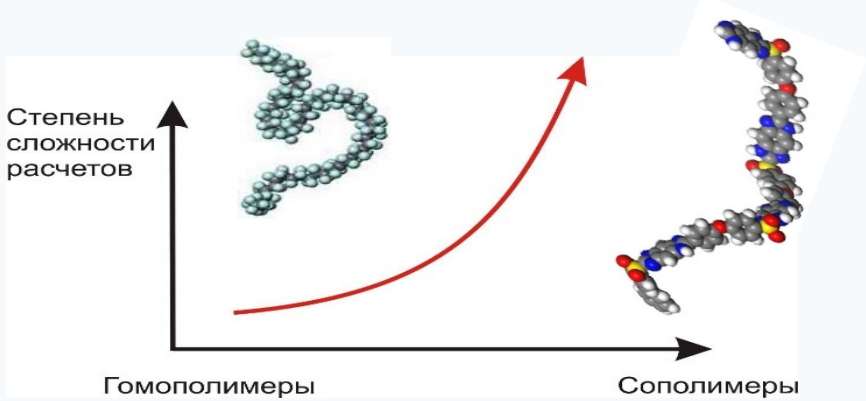
prediction of polymer properties based on regression models

The complexity of atomistic simulations



$$Yj = A0 + A1 \cdot x1,j + \cdots + Ap \cdot xp,j$$

An alternative way to predict properties is QSPR regression models

A.A. Askadskii

Bicerano

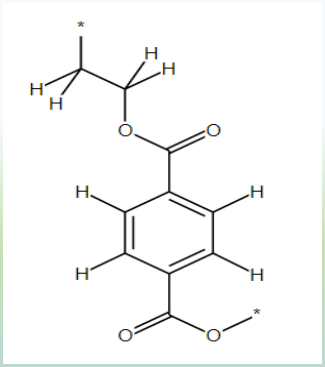
Van-Krevelen

Oxygen permeability model in the Biczerano model

$\ln(P_{O2}) = 8.515520 - 0.017622 * v$

$v = E_{Coh1}/V - 196 \cdot V/V_w + 110 \cdot N_{Rot}/N - 57 \cdot N_{Per}/N$

$N_{per} = 2 \cdot N_{C=C} - 14 \cdot (N_{bb\ ester}) + 5 \cdot X_{4'} - 7 \cdot N_{hheq\ \sigma} - 6 \cdot N_{cyanideeq\ \sigma} - 12 \cdot N_{hb,ar}$



Chemical structure

QSPR модель → P_{O2}

Physical properties

E_{Coh1} – cohesive energy;

V - molecular volume;

Vw – van der Waals volume;

N_{rot} - number of rotation bonds;

N - number of non-hydrogen atoms;

$N_{C=C}$ – number of acyclic carbon-carbon double bonds;

$N_{bb\ ester}$ - number of ester groups in the main chain;

$X_{4'}$ - number of substituents in aromatic rings in the main chain;

$N_{hheq\ \sigma}$ - sum of Cl+Br atoms attached to sp3 carbon atoms;

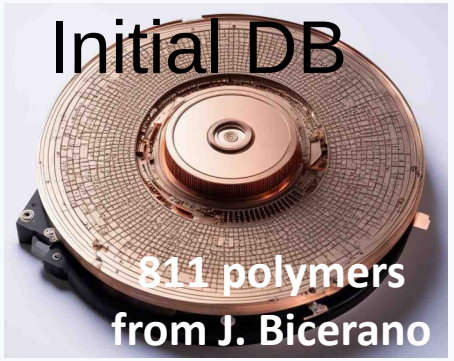
$N_{cyanideeq\ \sigma}$ – sum of cyanide groups attached to sp3 carbon atoms;

$N_{hb,ar}$ - number of hydroxyl hydrogen atoms and aromatic rings, hydrogen bond

quantitative structure-property relationship model

PROPERTY
QSPR

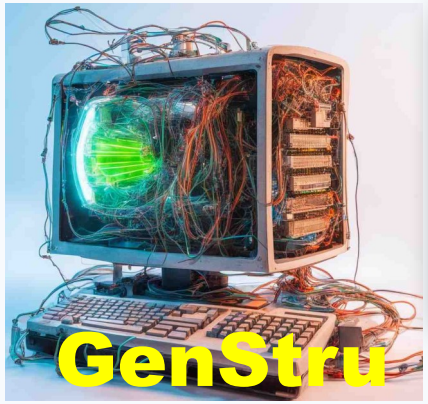
GenStruc program for generating
the new polymer SRUs using the enumeration and Monte Carlo algorithms.

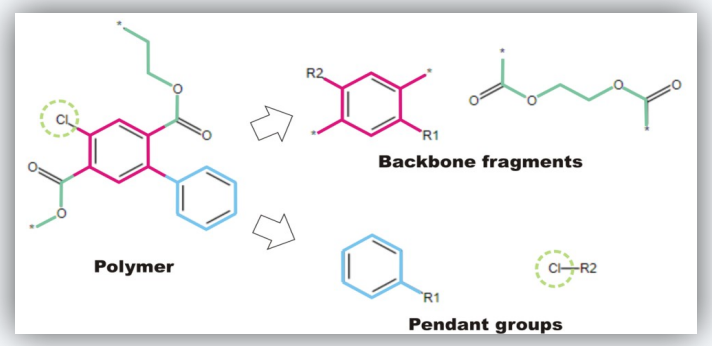


Backbone DB

Pendant DB

15M structs

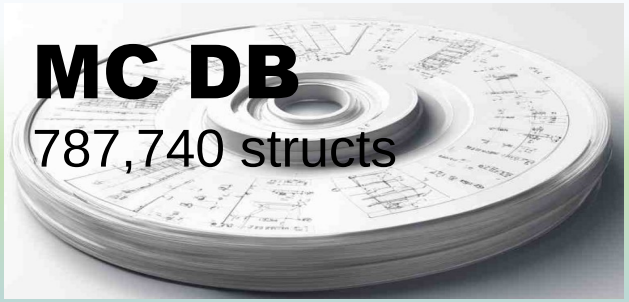


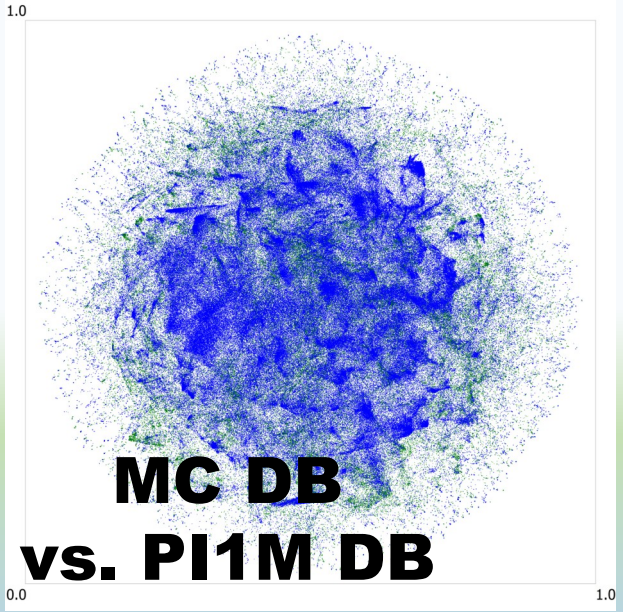


Enumeration algorithm

Monte-Carlo algorithm

+ DB FILTRATION





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Knizhnik, A. A. et al. // Nanomanufacturing 2023, 4, 1–26.

quantitative structure-property relationship model

PROPERTY
QSPR

PolyPred program for predicting properties for a given input polymer as well as for multiple structures stored in the database files.

✓ PROPERTIES PREDICTION USING BICERANO REGRESSION MODEL

Abbreviation	Property Name	Unit of Measure
CL	specific heat capacity, liquid	J/g/K
CS	specific heat capacity, solid	J/g/K
COH1	specific cohesion energy, Feudor	J/g
COH2	specific cohesion energy, Van Krevelen	J/g
DELTA1	delta solubility, Feudor	$(J/cc)^{0.5}$
DELTA2	delta solubility, Van Krevelen	$(J/cc)^{0.5}$
RLL	specific refraction	cc/g
PLL	specific polarizability	cc/g
MU	dipole moment	Debye
MB	bulk modulus	MPa
STIFFNESS	molar stiffness	$g^{0.25}cm^{1.5}/mole^{0.75}$
EPSILON	dielectric constant	
N	refractive index	
VISFUNC	molar viscosity	$gJ^{1/3}mole^{-4/3}$
EAFLOW	specific activation energy of viscous flow	kJ/g
O2PERM	permeability of oxygen	Barrers
N2PERM	permeability of nitrogen	Barrers
CO2PERM	permeability of carbon dioxide	Barrers
TDECOMP	decomposition temperature	K
SINF	brittle fracture stress at infinite mol weight	MPa
SIGMAF	brittle fracture stress at specified mol weight	MPa
SIGMAY	yield stress	MPa

Table 2. Predicted and experimental refractive indices of some polythiophene analogs.

Compound	Experimental Value	Bicerano [9]	Polymer Genome
polythiophene [*]c1ccc(s1)[*]	1.4 [67], 3.36 [65]	1.75	2.10 [14]
[*]c3ccc(Sc2ccc(Sc1ccc([*])cc1)cc2)cc3	1.75	1.68	1.72 [66]
[*]c3ccc(Sc2ccc(Sc1ccc([*])cc1)s2)cc3	1.75	1.71	1.77 [66]
[*]c3ccc(Sc2nnc(Sc1ccc([*])cc1)s2)cc3	1.75	1.71	1.71 [66]
[*]c5ccc(Sc4c19CCSc1c(Sc2ccc([*])cc2)c3SCCSc34)cc5	1.77	1.76	1.80 [14]

Table 3. Predicted dielectric constant values for some compounds.

Compound	Dielectric Constant		
	Figure 7g in Ref. [1]	Bicerano [11]	Polymer Genome [14]
Hydroxylamines			
-CO-NH-CO-NH-O-CH2-O-NH-	4.69	6.88	5.0
-NH-CO-NH-CO-O-NH-CO-O-CO-	4.71	5.77	5.3
-NH-O-NH-O-CH2-O-NH-CO-NH-CO-	4.61	6.82	4.9
-CO-O-CO-NH-CO-NH-CO-O-NH-CO-NH-	4.78	6.33	5.3
-NH-CO-O-CO-NH-O-CO-NH-CO-O-NH-CO-	4.65	5.65	5.2
Hydrazides			
-NH-CO-NH-		7.84	5.3
-NH-CO-NH-CO-NH-		8.04	5.4
-NH-CO-NH-CO-NH-NH-CO-		8.12	5.5

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conclusion

- The **MULTICOMP** software package enables predictive calculations of the properties of polymer matrix nanocomposites based on multilevel modeling, including:
  - Determination of the structure of composites, distribution of the filler in the matrix
  - Determination of Effective Macroscopic Properties of the Whole Composite
- The **MULTICOMP** package allows one to create flexible calculation scenarios using high-performance computing resources, providing automatic data transfer and control over the execution of calculations
- The **MULTICOMP** package can be used both for the practical development of new materials and for teaching students methods of computational materials science.
- The **MULTICOMP** software package is an open platform that implements the ***Scientific Workflow*** concept and allows users to create their own calculation scenarios and add new calculation modules

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areas of practical application MULTICOMP

- Predicting the properties of polymer matrices depending on the chemical structure of monomers
- Prediction of changes in the glass transition temperature of a polymer matrix upon the introduction of a nanoscale filler
- Predicting changes in the mechanical properties of polymer matrices upon the introduction of a nanoscale filler (hardening of plastic, changing the properties of rubber products)
- Predicting changes in the thermal conductivity of polymer matrices upon the introduction of a nanoscale filler (insulating materials, membranes)
- Predicting changes in the gas permeability of polymer matrices upon the introduction of a nanoscale filler (film, membrane)

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application of MULTICOMP in education

- The developed package can be used both for the practical development of new materials and for teaching students methods of computational materials science.
- With the help of **MULTICOMP**, students can master the basics of atomistic and mesoscopic modeling of polymer systems without the need to study specific modeling programs and direct work with remote computing resources (creating computer classes)
- Based on **MULTICOMP**, laboratory workshops can be developed for the introduction of composite materials based on polymer matrices with organic and inorganic fillers into physics and chemistry.
- Also, this Package can be useful for teaching the basics of multilevel modeling of composite materials (end-to-end modeling from atomistics to the macrolevel)

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acknowledgments

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  - суперкомпьютерного комплекса Московского государственного университета имени М.В. Ломоносова

thank you for the attention

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