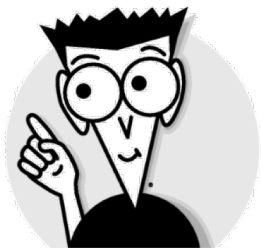
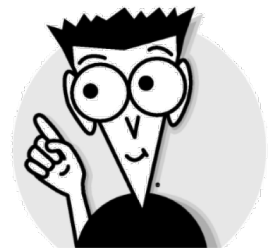
Simulazione Molecolare

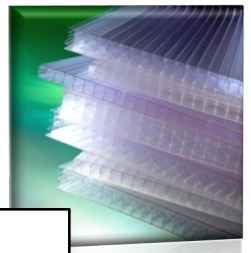
A.A. 2019-2020

Utilizzo dei metodi agli Elementi Finiti per lo studio di materiali nanocompositi



SIMULAZIONE MULTISCALA





TEMPI CARATTERISTICI

years
hours
minutes
seconds
microseconds
nanoseconds
picoseconds
femtoseconds

Morfologia
Miscibilità e compatibilità
Fenomeni di diffusione
Stabilità strutturale
Tensione superficiale
Fenomeni di aggregazione e coagulazione

Engineering design

Process simulation

FEM

Mesoscale modeling (groups of atoms or molecules)

Molecular mechanics (atoms)

Quantum mechanics (electrons)

Dissipative Particle Dynamics

Mesodyn

1Å 1nm 1μm 1mm 1m

LUNGHEZZE CARATTERISTICHE

POLIMERI NANOCOMPOSITI

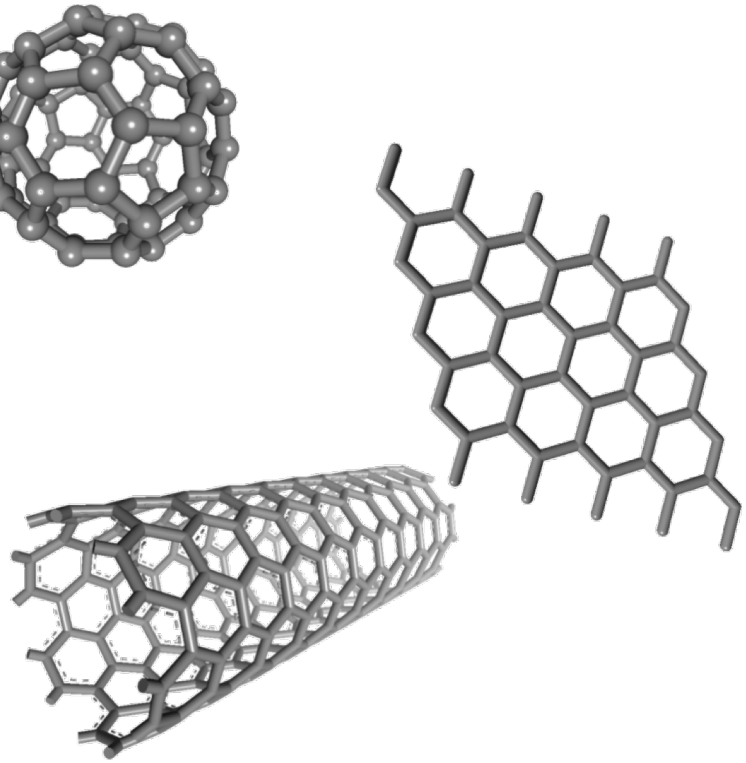
DEFINIZIONE

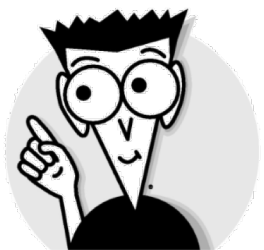
Combinazione di una matrice polimerica e inclusioni che hanno almeno una dimensione (lunghezza, profondità, spessore) nella scala nanometrica.

nanoparticelle ⟶ 3D

nanosheets ⟶ 2D

nanowires ⟶ 1D





Perchè i nanocompositi?

I tradizionali materiali compositi hanno delle dimensioni micrometrica

Le interazioni molecolari tra polimero e nanofillers daranno un materiale nanocomposito innovativo con proprietà ottimizzate rispetto ai materiali convenzionali

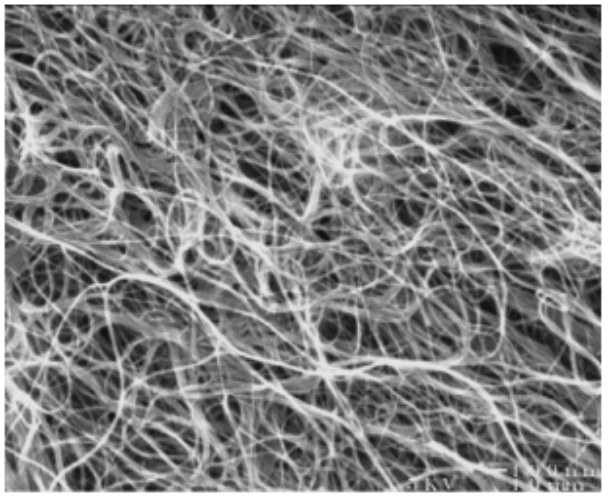
Alla scala nanometrica, le proprietà diventano dimensioni-dipendenti

Perché dovremmo aspettarci miglioramenti?

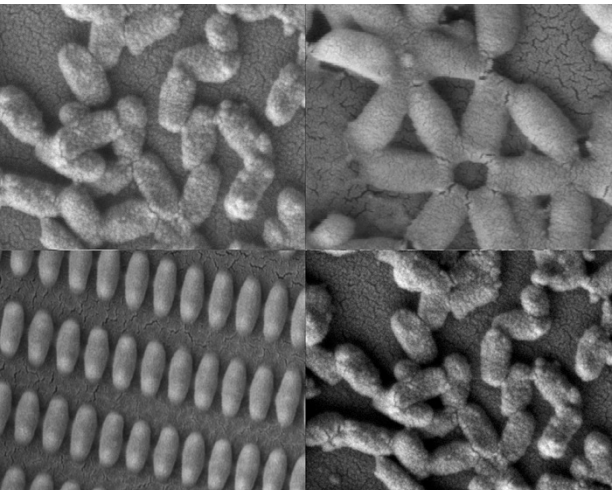
- Un aspetto unico della nanotecnologia è il rapporto notevolmente aumentato tra area superficiale e volume presente in molti materiali su scala nanometrica
- Esempio: le platelets di montmorillonite (nanoclay) hanno un'area superficiale di 75 m^2/g. Ciò significa che ~7g di platelets possono coprire un'area delle dimensioni di un campo di calcio
- L'enorme superficie si traduce in pratica nel fatto che la matrice polimerica sarà costantemente in contattato nel composito con la nanoparticella
- Poiché le proprietà fisiche delle nanoparticelle stesse sono generalmente superiori alla matrice polimerica, ciò suggerisce che **le proprietà del nanocomposito tenderanno a quelle delle nanoparticelle**

POLYMER MATRICES

- Thermoplastic resins: PS (10%), PVC (2%), PP (13%), PA6 (12%), PMMA (5%), PE (4%), PEO, PVA; ……
- Thermoset resins: phenolic, epoxy, ……
- Elastomers: PI, natural and synthetic rubber, ……



Entangled CNTs



FILLERS

- Montmorillonite organoclays (MMT)
- SiO_2, TiO_2, Au, Fe_xO_y, ……
- Carbon nanotubes (CNTs)
- Carbon or Glass fibers
- Others

POLYMER NANOCOMPOSITES properties

Advantages

- Low filler content (2-5%wt) → High performances & good processability
- Good structural and functional properties

Depend on: matrix, nanofillers, …

Disadvantages

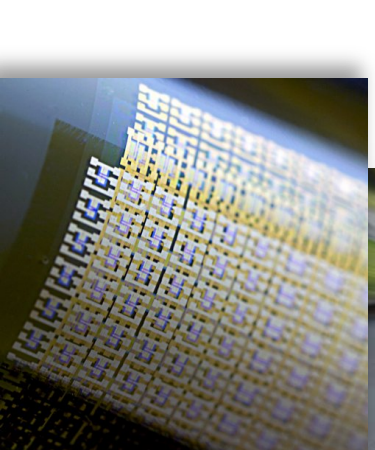
- Viscosity increase (limits processability)
- Dispersion and distribution difficulties

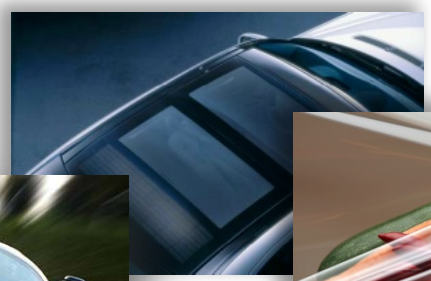
Improved properties

- Mechanical properties (tensile strength, stiffness, toughness)
- Gas barrier
- Flame retardancy
- Dimensional stability
- Thermal expansion
- Thermal conductivity
- Chemical resistance

applications

- Automotive (gasoline tanks, bumpers, interior and exterior panels, …)
- Building
- Electronics and electrical (printed circuits, electric components)
- Cosmetics (controlled release of “active agents”)
- Dentistry (filling materials)
- Environment (biodegradable materials)
- Gas barrier films
- Military, aerospace and commercial applications
- Thin film photovoltaic circuits





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MOSE Molecular Simulation Engineering enabling innovation

POLITECNICO DI TORINO

CTU CZECH TECHNICAL UNIVERSITY IN PRAGUE

LUXEMBOURG INSTITUTE OF SCIENCE AND TECHNOLOGY

LIST

INSA INSTITUT NATIONAL DES SCIENCES APPLIQUÉES LYON

eXstream ENGINEERING

GRANTA MATERIAL INTELLIGENCE

esi get it right®

AIRBUS

DOW®

ESTECO

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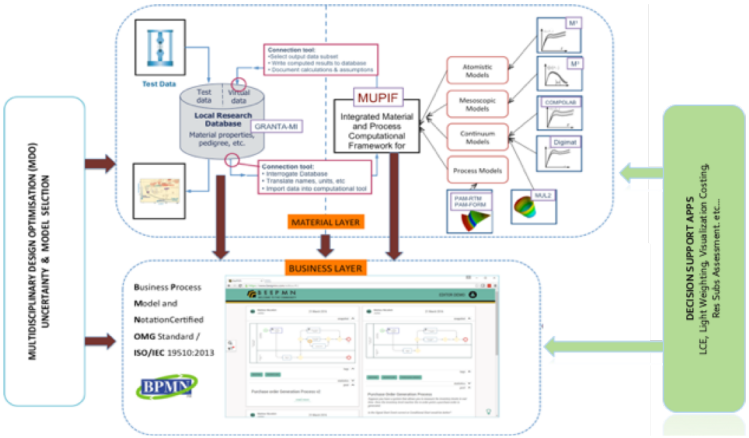
- The mission of COMPOSELECTOR is to develop a Business Decision Support System (**BDSS**)
- Integrating **materials modelling**, business tools and databases into a single workflow
  - **Material selection** and **design** of polymer-matrix composites (**PMCs**)
- Taking in account the implementation costs, associated risks, uncertainties and costs related to the modelling and simulation
- Predicting relevant properties and **Key Performance Indicators** (KPIs), accounting for material internal microstructure and effects of processing
- Accuracy/validation of predicted data, and relevant management of uncertainty
- The BDSS generate a decision on the models to be used, seen the balance investment (staffing, run-time versus return, accuracy, trend prediction…)



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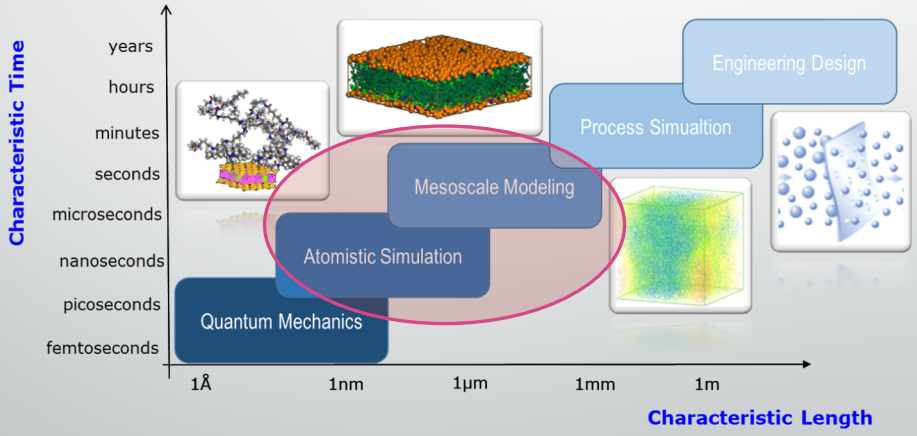
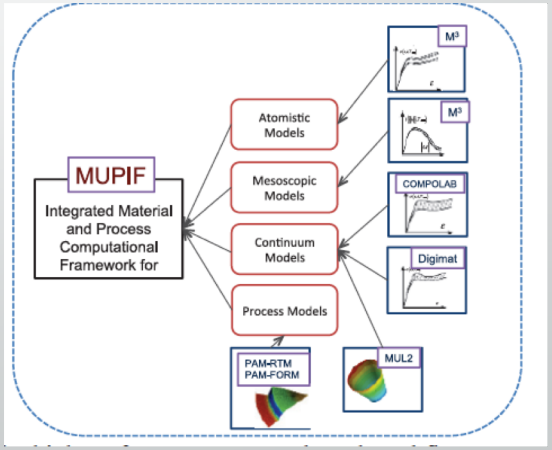
- Airbus:
  - ✓ selecting materials and manufacturing process for aerospace applications.
  - ✓ Matrix: semicristalline thermoplastic polymer; Reinforcement: carbon nanofiber and/or CNT
  - ✓ KPI : Manufacturing, Light weighting ,Costing, Sustainability (green design and Life cycle engineering requirements) Supply chain requirements.
- DOW:
  - ✓ selecting materials and manufacturing process for automotive applications.
  - ✓ Matrix: different epoxy resins (thermoset); Reinforcement: glass or carbon fibers
  - ✓ KPI : Production target, Design requirements, Light weighting,Costing, Manufacturing.
- GOODYEAR:
  - ✓ selecting materials and manufacturing process for tires.
  - ✓ Matrix: Polybutadene + Polyisoprene (rubber); Filler: carbon or silica particles; Coupling agent: Silanes
  - ✓ KPI : Mechanical response, costing, weighting.

Multi-scale Molecular Modeling

- **Atomistic**
- **Coarse-grained**
- Continuum model
- Process Model





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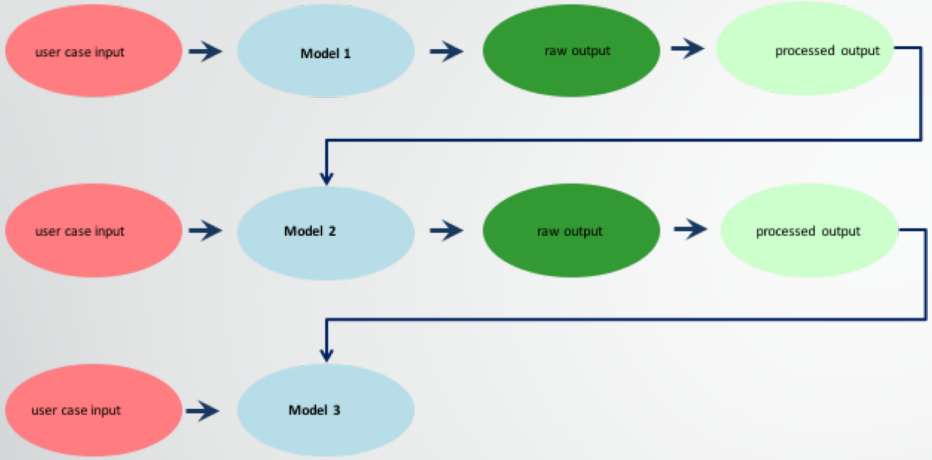
- Developing computational recipes and workflow, general and software **independent**
- Both atomistic and coarse-grained/mesoscopic scales are involved
- Developing computational **workflows** and relevant recipes for obtaining the following properties:
  - ✓ Mechanical Properties (Atomistic MD + Coarse-grained):
    - Stress-strain behaviour curves
    - Mechanical moduli and constants (E, K, G, Poisson ratio, Lamè constants, and linear elastic constant)
  - ✓ Interfacial properties (Atomistic MD):
    - Interaction energies between matrix and filler (atomistic MD to Coarse-grained)
    - Density
  - ✓ Rhelogical properties (Atomistic MD + Coarse-grained):
    - Storage and loss Moduli
- Estimation of **business parameters** for the developed computational procedures

Moda Form



- **RoMM** : Review of Materials Model
- concepts and proposes names which harmonise the language of modelling
- **common language** to foster dialogue between industrial end-users, software developers and researchers
- harmonised language using the **MODA** template.

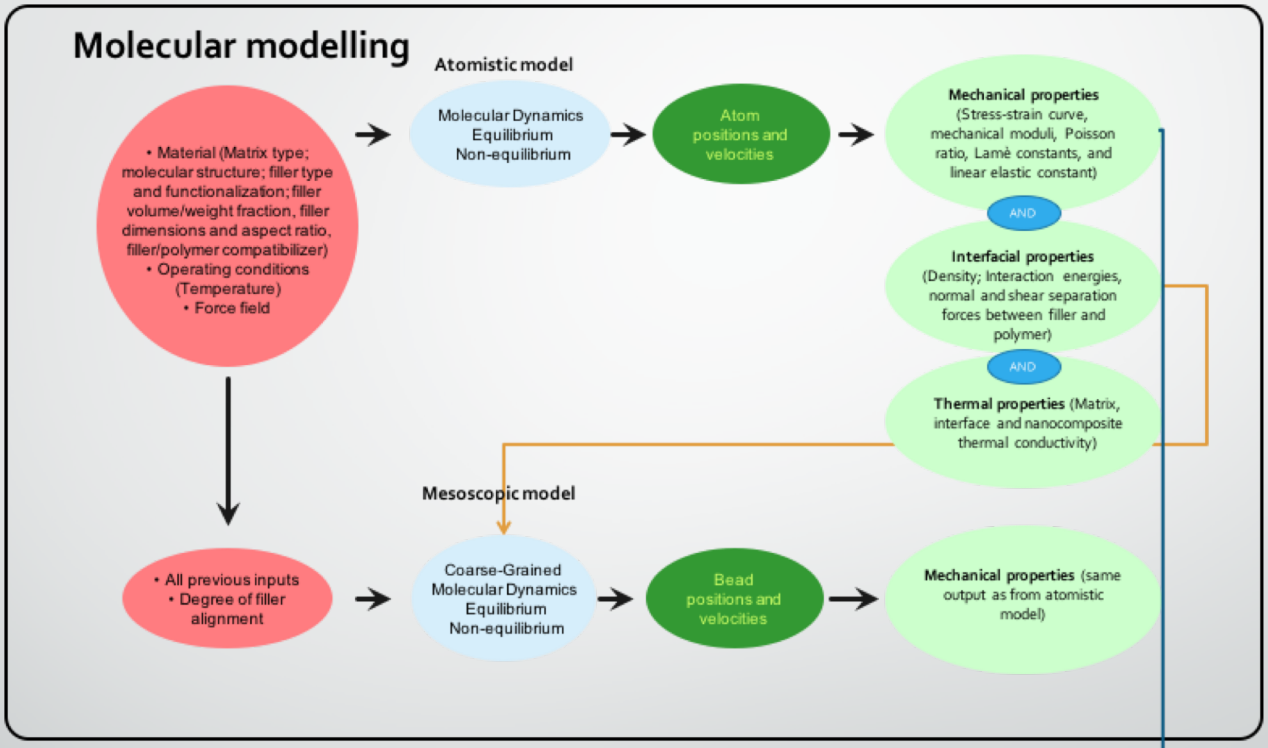
1	Aspect of the User Case/System to be Simulated	
1.1	Aspect of the User Case to be simulated	*Describe the aspects of the User Case textually.* *No modelling information should appear in this box. This case could also be simulated by other models in a benchmarking operation! The information in this chapter can be end-user information, measured data, library data etc. It will appear in the pink circle of your workflow picture.* *Simulated input which is calculated by another model should not be included (but this input is listed in chapter 2.4)* *Also the result of pre-processing necessary to translate the user case specifications to values for the physics variables of the entities can be documented here.*
1.2	Material	*Chemical composition, ...*
1.3	Geometry	*Size, form, picture of the system (if applicable)* *Note that computational choices like simulation boxes are to be documented in chapter 3.*
1.4	Time Lapse	*Duration of the User Case to be simulated.* *This is the duration of the situation to be simulated. This is not the same as the computational times to be given in chapter 3.*
1.5	Manufacturing process or in-service conditions	*If relevant, please list the conditions to be simulated (if applicable).* *E.g. heated walls, external pressures and bending forces.* *Please note that these might appear as terms in the PE or as boundary and initial conditions, and this will be documented in the relevant chapters.*
1.6	Publication on this data	*Publication documenting the simulation with this single model and its data (if available and if not already included in the overall publication).*

2	Generic Physics Of The Model Equation		
2.0	Model type and name		*Model type and name **chosen from RoMM content list** (the PE).* *This PE and only this will appear in the blue circle of your workflow picture. Please do not insert any other text although an indication of the MR is allowed.*
2.1	Model entity		*The entity in this materials model is <finite volumes, grains, atoms, or electrons>*
2.2	Model Physics/ Chemistry equation PE	Equation	*Name, description and mathematical form of the PE* *In case of tightly coupled PEs set up as one matrix which is solved in one go, more than one PE can appear.*
		Physical quantities	*Please name the physics quantities in the PE, these are parameters (constants, matrices) and variables that appear in the PE, like wave function, Hamiltonian, spin, velocity, external force.*
2.3	Materials relations	Relation	*Please, give the name of the Material Relation and which PE it completes.*
		Physical quantities/ descriptors for each MR	*Please give the name of the physics quantities, parameters (constants, matrices) and variables that appear in the MR(s)*
2.4	Simulated input		*Please document the simulated input and with which model it is calculated.* *This box documents the interoperability of the models in case of sequential or iterative model workflows. Simulated output of the one model is input for the next model. Thus what you enter here in 2.4 will also appear in 4.1 of the model that calculated this input.* *If you do simulations in isolation, then this box will remain empty.* *Note that all measured input is documented in chapter 1 "User Case".*

3	Solver and Computational translation of the specifications		
3.1	Numerical Solver		*Please give name and type of the solver.* *E.g. Monte Carlo, SPH, FE, ...iterative, multi-grid, adaptive,...*
3.2	Software tool		*Please give the name of the code and if this is your own code, please specify if it can be shared with an eventual link to a website/publication.*
3.3	Time step		*If applicable, please give the time step used in the solving operations. This is the numerical time step and this is not the same as the time lapse of the case to be simulated (see 1.4)*
3.4	Computational Representation	Physics Equation, Material Relations, Material	*Computational representation of the Physics Equation, Materials Relation and material.* *There is no need to repeat User Case info. "Computational" means that this only needs to be filled in when your computational solver represents the material, properties, equation variables, in a specific way.*
3.5	Computational boundary conditions		*If applicable.* *Please note that these can be translations of the physical boundary conditions set in the User Case or they can be pure computational like e.g. a unit cell with mirror b.c. to simulate an infinite domain.*
3.6	additional Solver Parameters		*Please specify pure internal numerical solver details (if applicable), like* • *specific tolerances,* • *cut-off, convergence criteria* • *integrator options*

4	POST PROCESSING	
4.1	The processed output	*Please specify the output obtained by the post processing.* *If applicable then specify the entity in the next model in the chain for which this output is calculated: electrons, atoms, grains, larger/smaller finite volumes.* *In case of homogenisation, please specify the averaging volumes.* *Output can be calculated values for parameters, new MR and descriptor rules (data-based models).*
4.2	Methodologies	*Please describe the mathematics and/or physics used in this post-processing calculation.* *In homogenisation this is volume averaging. But also physics equations can be used to derive e.g. thermodynamics quantities or optical quantities from Quantum Mechanics raw output.*
4.3	Margin Of Error	*Please specify the margin of error (accuracy in percentages) of the property calculated and explain the reasons to an industrial end-user.*

Moda Form – Case study 1



Other Models or DataBase

EU-Project "COMPOSELECTOR" AIRBUS CASE

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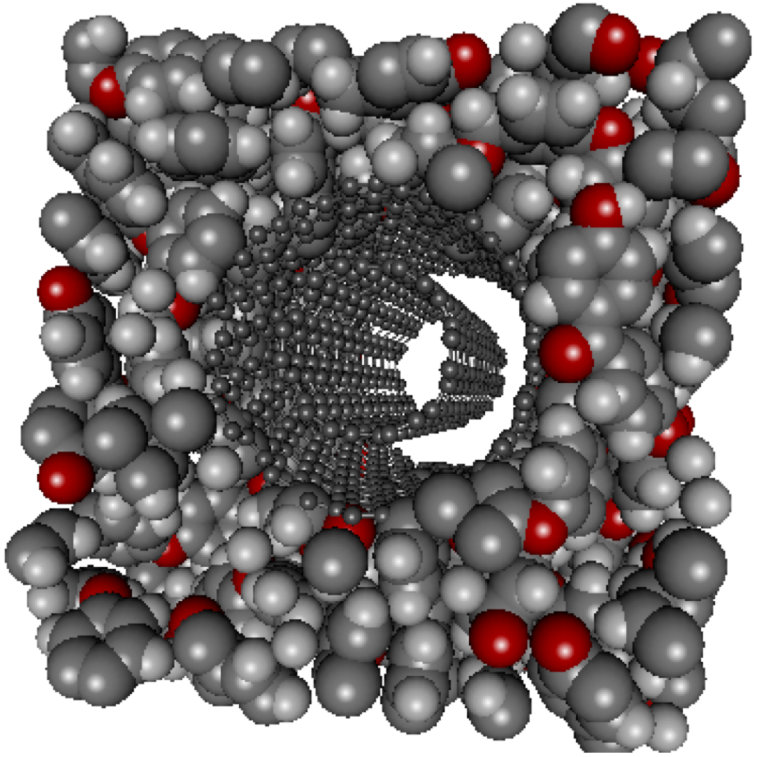
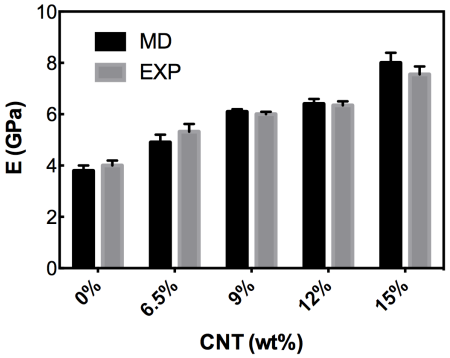
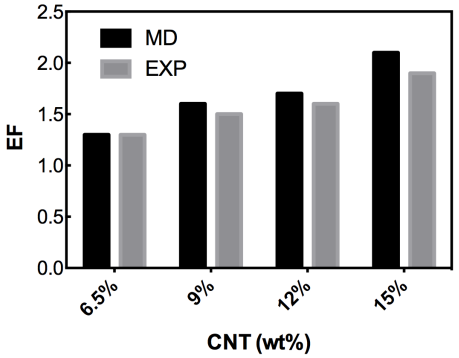
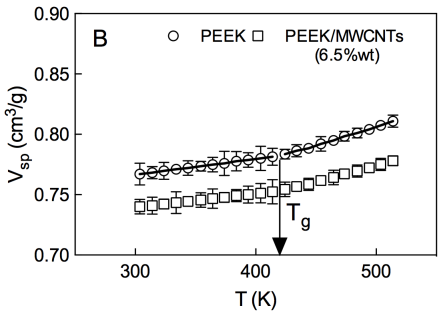
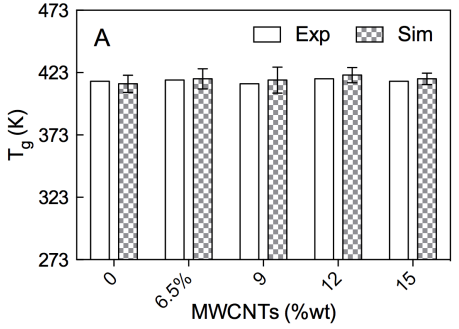
- Polymer matrix: PEEK (thermoplastic); Reinforcement: MWCNT
- Mechanical properties → increment of the Young's Modulus
- Thermal properties → stabilized Tg











EU-Project "COMPOSELECTOR" DOW CASE

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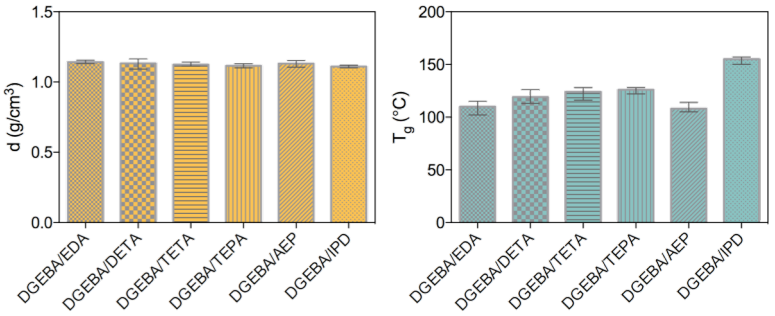
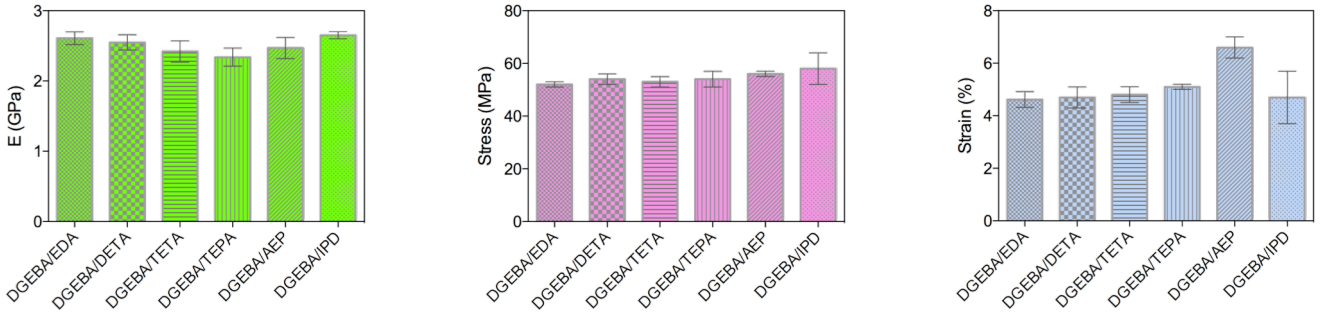
- ρ (@RT°), T_g and mechanical properties= f(hardener); fully cured (85%)
- Model: atomistic simulations
- Model system considered: DGEBA (thermoset) + ≠ hardener



Density at 25°C (left) and T_g (right) as function of different curing agents



Young's modulus (E, GPa, left), Stress (MPa, center), and Strain (%, right) values as function of different curing agents

EU-Project "COMPOSELECTOR" GOODYEAR CASE

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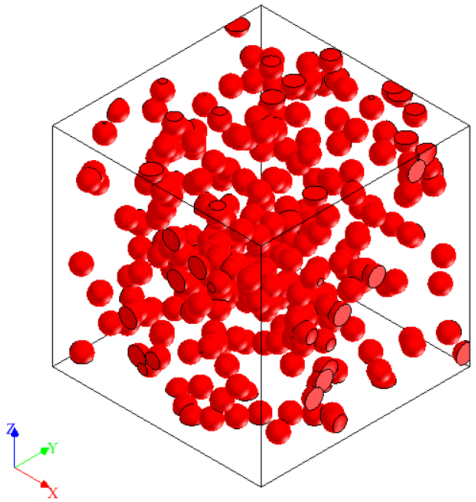
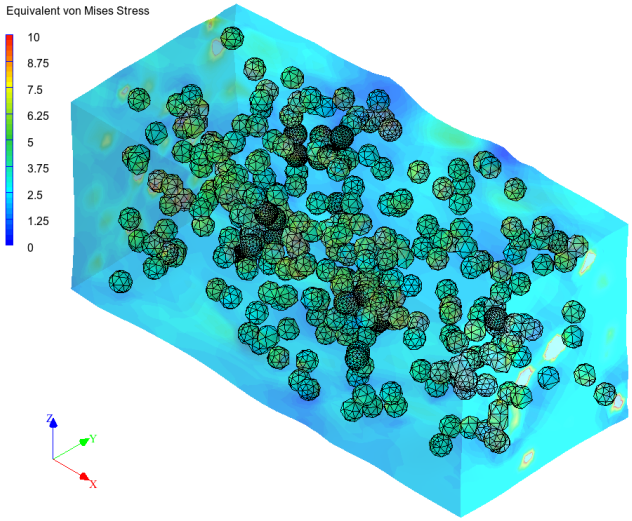
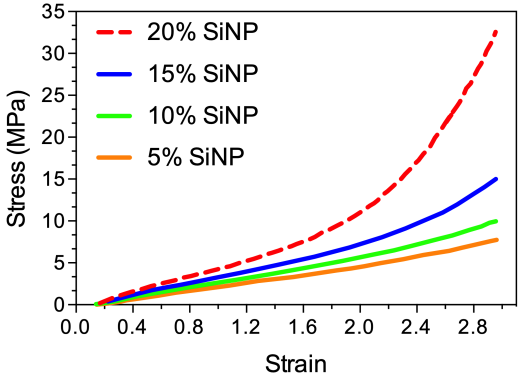
- Morphology of the NP dispersion in a rubber matrix
- Model: DPD + continuum simulations
- Model system considered: SBR rubber + functionalized SiO_2 nanoparticles







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COMPUTATIONAL BUSINESS PARAMETERS

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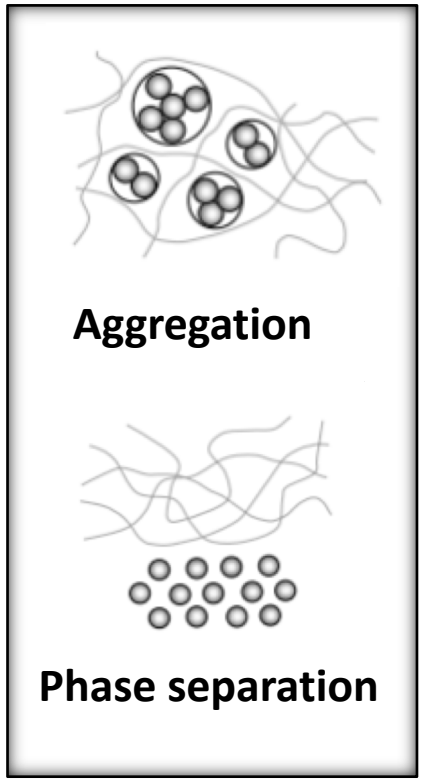
AIRBUS CASE							
"Model System"	**Material Property**	**Model**	**KPI**	**Reliability**	**Personnel Cost**	**Computational Cost**	**Benefit**
PEEK + MWCNTs	Density	Atomistic	weight reduction or no weight increase	2-3 %	32 €	1.20 €	Time, cost, T_g (bonus)
PEEK + MWCNTs	Mechanical properties	Atomistic	no change (worsening) in mechanical properties	7-10 %	64 €	3.20 €	Time, cost
PEEK + MWCNTs	Interfacial properties	Atomistic	no specific KPI but correlated to strength	NA	96 €	1.60 €	Time, cost, F_{po} and F_{coh} very hard to measure
PEEK + MWCNTs	Thermal Conductivity	Atomistic + Mesoscopic	no specific KPI but requested as a property	5-7%	768 €	115 €	F(≠ fiber orientation), useful for very costly materials design

Keys to nanocomposites polymers

- Purtroppo i nanofiller sono raramente compatibili con le matrici polimeriche e una quantità enorme di tempo, denaro e sforzi è stata impiegata nel tentativo di superare questo problema.
- Se il nanofiller non agisce a livello di nanometri, non dovremmo davvero aspettarci risultati diversi da quelli ottenuti con un normale filler macroscopico

2

1



polymer

+

layered silicate

=

conventional composite

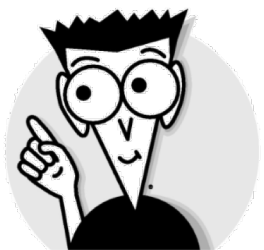
intercalated composite

exfoliated composite

Keys to nanocomposites polymers

- **Compatibilità**: i nanofillers devono avere compatibilità con la matrice
- **Dispersione**: se si ottiene una buona compatibilità, dovrebbe verificarsi una completa dispersione a livello molecolare/nano
- **Proprietà**: se si ottiene la dispersione a livello molecolare/nano, si dovrebbero ottenere migliori proprietà ottiche, fisiche e meccaniche

Compatibility → Dispersion → Improved Properties



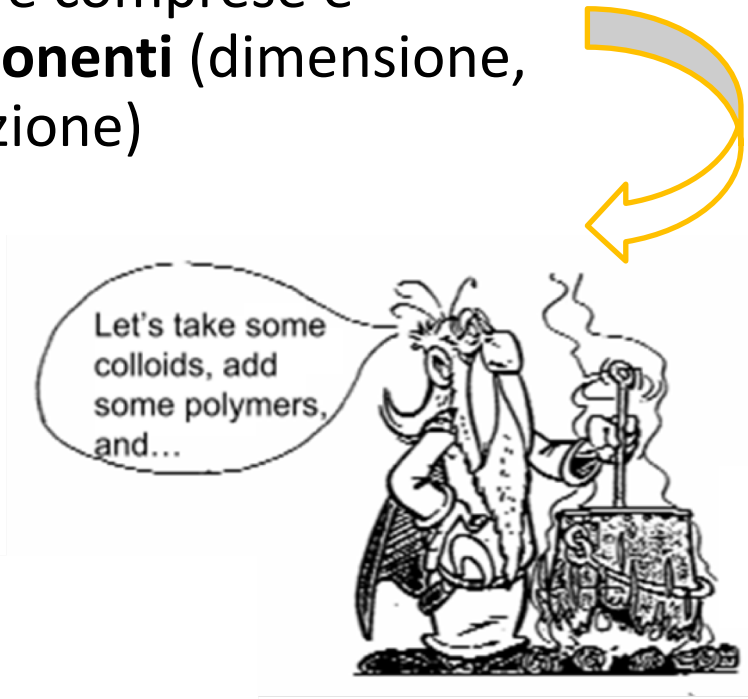
Keys to nanocomposites polymers

- **Proprietà** dipendono da:
  - la morfologia dei component
  - La struttura locale → **interazioni polimero/filler**!
- Le interazioni particella-particella, polimero-polimero, particella-polimero devono essere comprese e controllate **in funzione dei componenti** (dimensione, forma, composizione, concentrazione)

It's not a good strategy …

↓

MULTISCALE MODELING is better!!



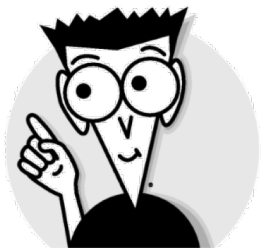
FINITE ELEMENT ANALYSIS (FEA) or FINITE ELEMENT METHOD (FEM)

What is FEA?

L'analisi degli elementi finiti (FEA) è un metodo numerico per risolvere problemi di ingegneria, fisica e matematica

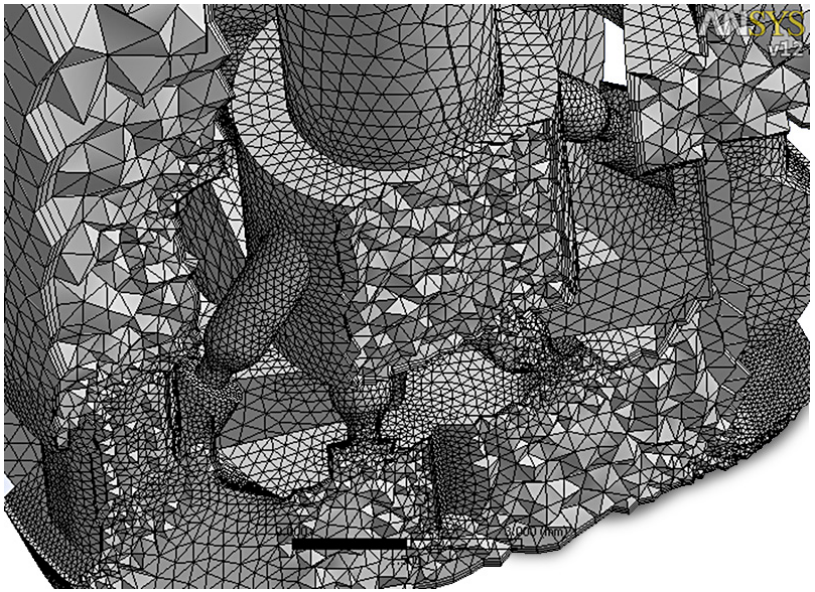
Why FEA?

- Utile per problemi con geometrie complicate, carichi e **proprietà dei materiali** in cui non è possibile ottenere soluzioni analitiche
- Può essere applicate in:
  - meccanica strutturale, fluidica, trasferimento di calore, elettricità e magnetismo e altri vari problemi complessi



FEA vs. ANALYTICAL METHODS

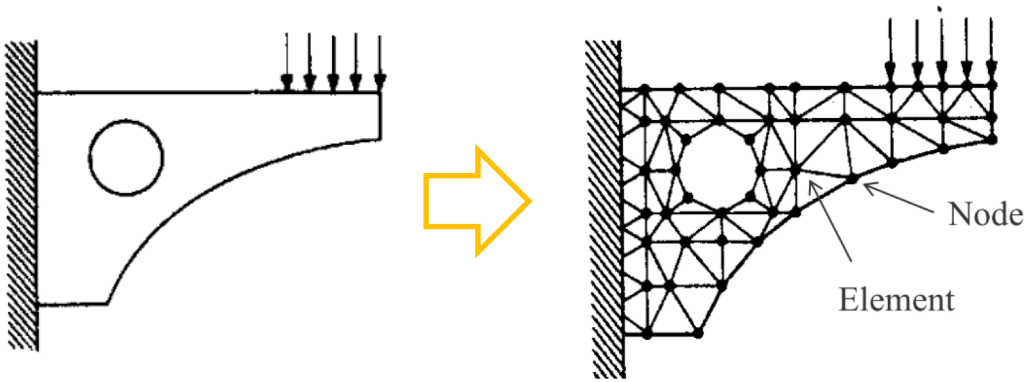
- I metodi analitici comportano la risoluzione dell'intero sistema in un'unica operazione
- FEA prevede la definizione di equazioni per ciascun elemento e la loro combinazione per ottenere una soluzione di sistema
  - – è quindi una tecnica di approssimazione

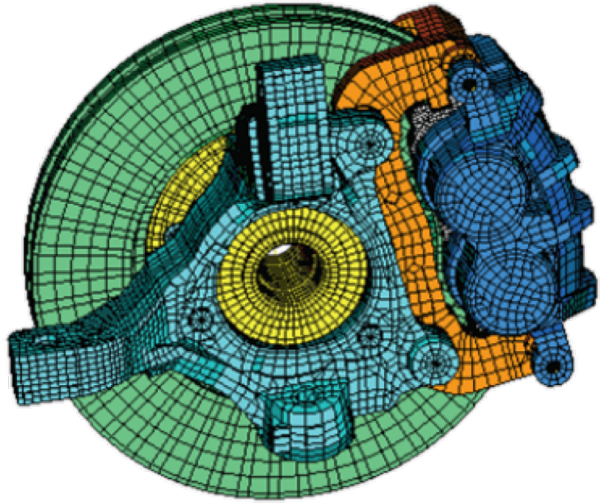


Divide and conquer!

- Le equazioni lineari semplici non sono valide su **larga scala** per parti con geometria complessa ma possono essere valide per una piccola regione di materiale all'interno della parte complessa.

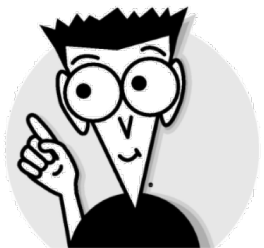
- Se suddividiamo un oggetto fisico complesso in un numero grande ma **finito di piccoli pezzi** (elementi) per i quali è possibile risolvere equazioni semplici con una precisione accettabile, quindi ricostruirne la struttura, possiamo creare una **soluzione significativa per l'intero** oggetto complesso



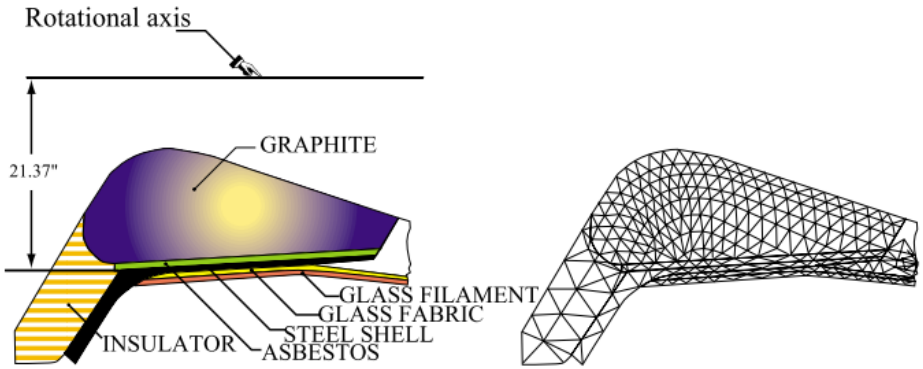


BASICS OF FINITE ELEMENT ANALYSIS

- Sostituire la geometria continua con un insieme di oggetti con un numero finito di gradi di libertà (**DOF**) → **MESHING**
- Dividi il corpo in un numero finito di unità più semplici con forme diverse → **ELEMENTI**
- Elementi connessi a punti nodali → **NODI**
  - punti comuni a due o più elementi adiacenti
  - insieme di elementi denominati "**mesh**"



Rocket Nozzle (Aerospace Engrg)



(a) Typical solid rocket nozzle (Aerojet Corp., 1963)

(b) Finite element idealization

Structural FEM

- I problemi strutturali sono definiti in termini di:
  - *carichi* (forza)
  - *resistenza alla deformazione*(stiffness)
  - *spostamenti*

- Data la semplice relazione: $\{\mathbf{F}\} = [k]\{\mathbf{d}\}$

  $\{\mathbf{F}\}$ = vettore delle forze applicate (una per ciascun DOF) è "nota" (carichi)

  $[K]$ = matrice di stiffness (DOFxDOF) è "nota"

  $\{\mathbf{d}\}$ = vettore degli spostamenti (una per ciascun DOF) **è da determinare**(spostamenti)

- Una volta noti gli spostamenti {d}, è possibile determinare le deformazioni e le sollecitazioni (stress-strain)

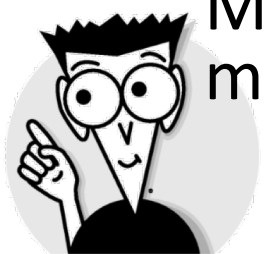
Basics of finite element methods

- *3 steps*:
  - **Pre-processing → *connessione con i modelli alle scale atomistiche e mesoscopica!!!***
    - Definire gli elementi
    - Definire le proprietà dei materiali degli elementi
    - Definire le proprietà geometriche degli elementi
    - Definire la connettività tra gli elementi(meshing)
  - Definire i vincoli fisici (BCs).
  - Definire i carichi
  - **Analysis**
    - Solver
  - **Post-processing**
    - Output dei dati FEA
    - Semplicità per la velocità nella progettazione
    - Molti sistemi supportano una visualizzazione grafica avanzata

Computer use in FEA

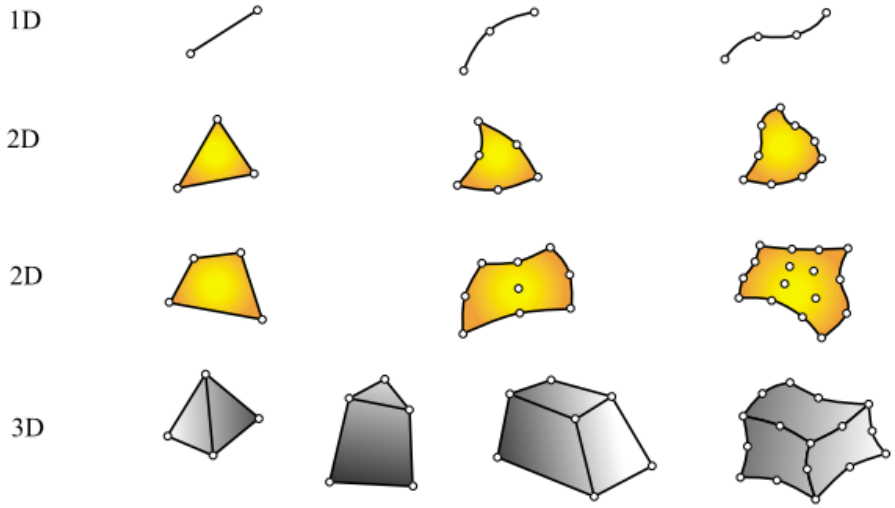
- Per queste ragioni:
  - - la natura relativamente semplice delle equazioni
  - - connettività tra elementi (risultanti da elementi adiacenti applicati)
  - - combinazione di soluzioni per singoli elementi
  - - il problema viene convertito in un gran numero di semplici equazioni algebriche da risolvere simultaneamente - richiede computer ad alta velocità
  - → FEA adatto per l'automazione computazionale

- DIGIMAT, Palmyra, Abaqus, ANSYS, COMSOL Multiphysics, ALGOR, NASTRAN, … and many many more!!!



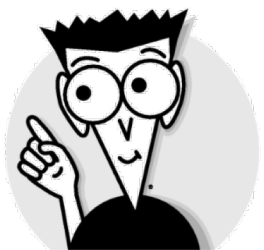
Mesh Element types

- La geometria dell'elemento è definita dalle posizioni dei nodi



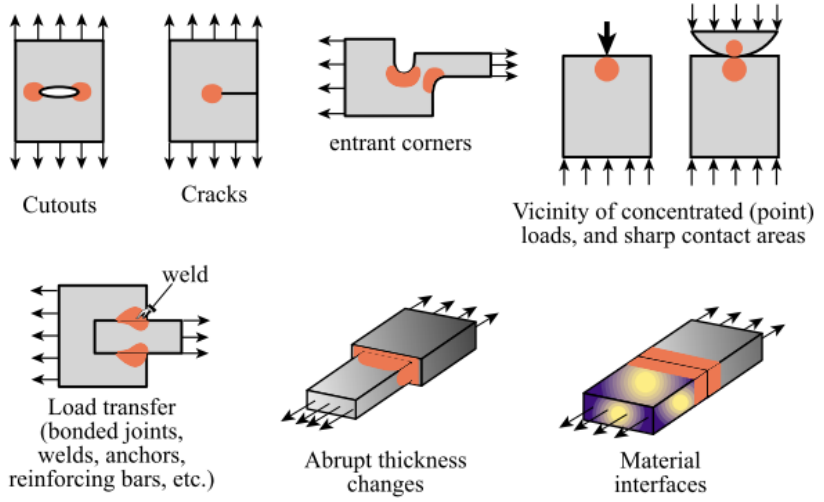
Gli elementi della mesh possono essere di diversi tipi: si avranno quindi elementi lineari, quadratici e cubi.

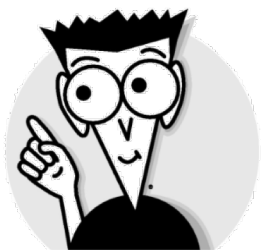
- La forma della mesh è fondamentale per l'analisi
- **Una maggiore densità migliora la soluzione a costo del tempo di calcolo**
- Una geometria semplice richiede meno elementi, una maggiore complessità richiede una maggiore densità
- La forma delle Mesh è correlata ai carichi, BCs, fenomenologia da simulare…..



WHERE FINER MESHES SHOULD BE USED

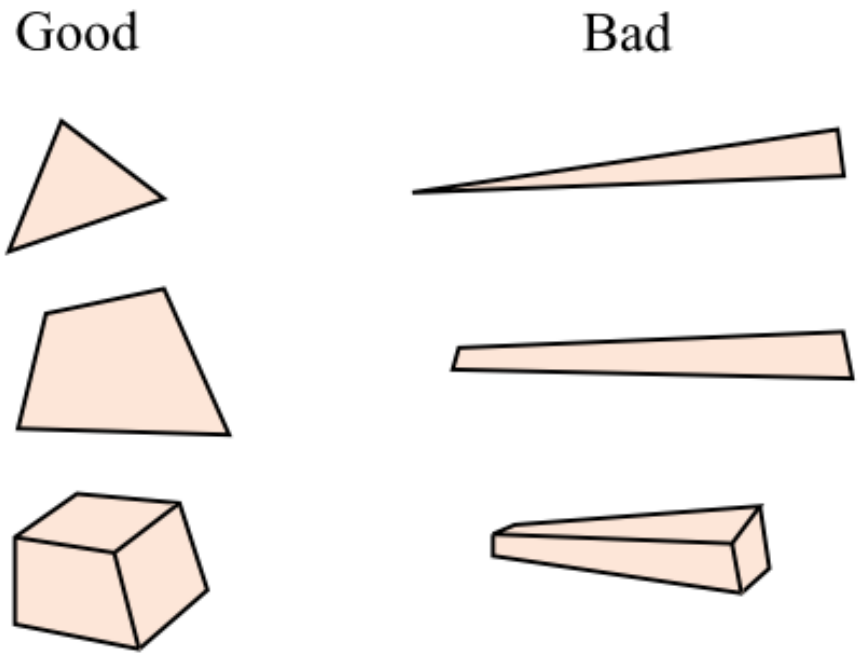
- I nodi individuano/definiscono i punti finali di tutti gli elementi 1D e gli angoli di tutti gli elementi 2D e 3D
- Poiché tutte le informazioni vanno nel modello e vengono calcolate per il modello a livello **nodale**, come minimo, i nodi devono essere presenti in tutte le posizioni in cui vi sono cambiamenti nella geometria o dove vi sono **carichi** applicati o **BCs** o all'**interfaccia** tra 2 materiali.

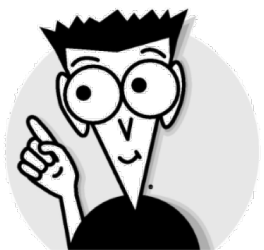




GOOD MESHING PRACTICE

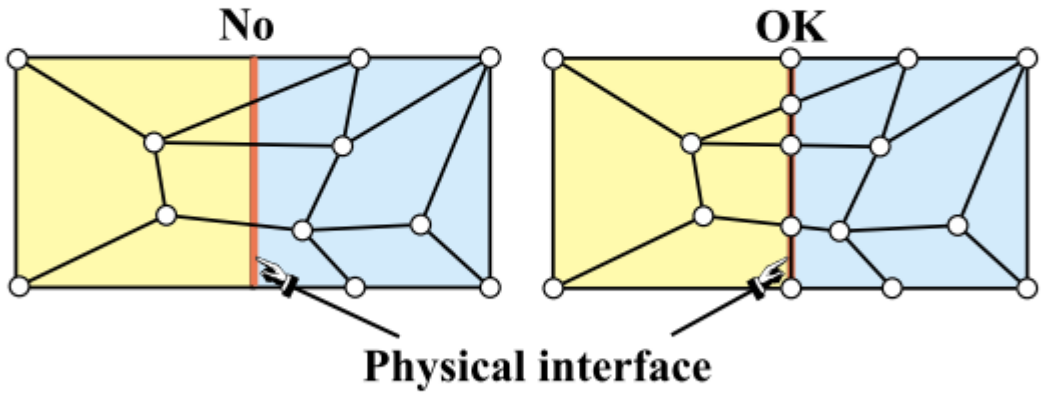
- Evitare elementi 2D/3D con proporzioni errate. Una buona mesh dovrebbe avere elementi ben modellati (proporzionali) e la transizione tra le differenti densità dovrebbe essere liscia e graduale senza elementi «affusolati» e distorti.





GOOD MESHING PRACTICE

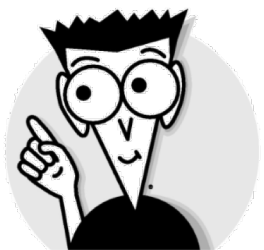
- all'interfaccia tra due materiali diversi, non possono esistere elementi che stiano in parte su un materiale e in parte sull'altro



- Preferenze della geometria degli elementi:

  A parità di altre condizioni, preferire

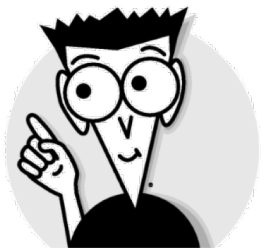
  - *In 2D*: quadrilateri rispetto ai triangoli
  - In *3D*: parallelepipedi rispetto cunei



GOOD MESHING PRACTICE

- Evitare elementi 2D / 3D con proporzioni errate
- *Mai, mai, mai* usare elementi complicati o particolari se non si è assolutamente sicuri di ciò che si sta facendo → difficoltà ad arrivare a convergenza del calcolo!
- Utilizzare la mesh più semplice possible in grado di descrivere i comportamenti dominanti del modello fisico, in particolare nelle situazioni di progettazione.

3 word summary: KEEP IT SIMPLE!



AVVERTENZE

- **Risultati buoni SOLO quando sarà buono il lavoro svolto nella creazione di mesh, nell'applicazione dei carichi e BCs**
  - se non calcolati e applicati correttamente, i risultati sono di scarsa utilità

An FEA program allows an engineer to make mistakes at a rapid rate of speed. (Miller)

An error caused by misunderstanding or oversight is not correctible by mesh refinement or by use of a more powerful computer. (Cook)