Representation of internal degrees of freedom in mesoscopic modeling of molecular systems, carbon nanotube materials... and metals

application to modeling of impact resistance of nanotube network materials

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Limitations of MD: Small time- and length-scales

Number of atoms \( \sim (\text{size of the system})^3 \)

Computational cost \( \sim (\text{number of atoms})^n \)

\( n > 1 \)
**Direct MD simulations is nanostructured materials**

(1) **MD simulations of individual structural elements** (nanofibers, nanoparticles, interfacial regions, grain boundaries, etc.) → difficult to predict macroscopic properties of nanomaterials

(2) **Direct large-scale MD simulations** of nanomaterials. Nanocrystalline materials - system with tens of nanograins (~$10^6$-$10^8$ atoms) can be simulated and the effective properties can be investigated, particularly in the regime of ultrafast mechanical loading (e.g. shock wave) or heating (e.g. by short laser pulse).
Direct MD simulations is nanostructured materials

Nucleation, growth, and coalescence of voids in dynamic failure in nanocrystalline Cu subjected to shock pulse loading.

Bridging the gap: The need for mesoscopic models

D. Qian et al., APL 76, 2868 (2000)

Hennrich et al., PCCP 4, 2273 (2002)

Phani et al., Acta Mater. 59, 2172 (2011)

Dislocation structures

CNT materials and CNT-polymer matrix nanocomposites

Phani et al., Acta Mater. 59, 2172 (2011)

Hennrich et al., PCCP 4, 2273 (2002)

D. Qian et al., APL 76, 2868 (2000)
Bridging the gap: The need for mesoscopic models

General strategy for designing mesoscopic models:

- identify the **relevant** collective degrees of freedom,
- design a mesoscopic force field for collective degrees of freedom,
- add additional rules to control behavior of the coarse-grained units.
Mesoscopic modeling of molecular systems, metals, and CNT materials far from thermal equilibrium

(shock waves, laser excitation, impact loading, particle bombardment, etc.)
Coarse-graining in modeling of molecular systems

Coarse-graining → reduces the number of degrees of freedom → increases time/length scales of simulations, but also... eliminates high-frequency vibrational modes

severe underestimation of the heat capacity, misrepresentation of thermal transport properties, dissipation of mechanical energy, etc.

This is not a problem if systems in the state of thermal equilibrium are of interest → various computational thermostats, fluctuation-dissipation theorem...

Tschöp et al., Acta Polymer. 49, 61, 1998


from fully-atomistic to united atom to massively coarse-grained
Coarse-graining in modeling of molecular systems

**Non-equilibrium phenomena** (shock waves, laser excitation, impact loading, particle bombardment, etc.) - the coarse-grained degrees of freedom are out of equilibrium with the ones eliminated by coarse-graining.

Matrix-assisted pulsed laser evaporation (MAPLE) technique for “gentle” deposition of thin polymer/biopolymer/nanocomposite films

Coarse-graining in modeling of molecular systems

Solvent: breathing sphere model
Polymer molecules: bead-and-spring model

Laser excitation and energy redistribution cannot be realistically represented → some rescaling of energy is needed, instantaneous local equilibration must be assumed

Local “heat path” approach:

1. introduce local “heat bath” description of thermal energy missing in the model
2. couple dynamic coarse-grained degrees of freedom to the local “heat bath” variables
3. pick strength of coupling based on rates of intra-/inter-molecular energy redistribution predicted in atomistic simulations or measured in pump-probe experiments
4. assign the capacity of the local “heat bath” based on experimental heat capacity
Coarse-graining in modeling of molecular systems

Solvent: breathing sphere model

Polymer molecules: bead-and-spring model

An additional dynamic “breathing mode” is added

The breathing mode is dynamically coupled (I) to translational degrees of freedom

The breathing mode is also connected to internal “heat bath” (II) with capacity based on experiment

\[ C^{\text{TR}} = 3k_B \]
\[ C^R = k_B \]
\[ C^{\text{HB}} = C^{\text{exp}} - C^{\text{TR}} - C^R \]

- The breathing mode serves as a “gate” for controlling the rate of the vibrational relaxation of excited molecules
- Experimental heat capacity is reproduced
Coarse-graining in modeling of molecular systems

Solvent: breathing sphere model

The breathing mode is dynamically coupled (I) to translational degrees of freedom

The breathing motion is controlled by an inertia parameter (or effective mass) $M_I$ ascribed to the corresponding breathing degree of freedom and an anharmonic potential:

$$U_R(R_i) = k_1(R_i - R_0)^2 + k_2(R_i - R_0)^3 + k_3(R_i - R_0)^4$$

$M_I = 32M_{BS}$

$k_1 = 10, k_2 = -20, k_3 = 20$
Coarse-graining in modeling of molecular systems

Solvent: breathing sphere model

The breathing mode is connected to internal “heat bath” (II) with capacity based on experiment

\[ C^{TR} = 3k_B \quad C^R = k_B \quad C^{HB} = C^{exp} - C^{TR} - C^R \]

\[ C^R \frac{dT^R_i}{dt} = A(T_i^{HB} - T_i^R) \]
\[ C_i^{HB} \frac{dT_i^{HB}}{dt} = -A(T_i^{HB} - T_i^R) \]

\[ \frac{d\Delta T}{dt} = -A \Delta T \left( \frac{C^R + C^{HB}}{C^R C^{HB}} \right) \]

\[ \Delta T = \exp \left( -\frac{t}{\tau} \right) \]
\[ \tau = \frac{1}{A \times \left( \frac{C^R + C^{HB}}{C^R C^{HB}} \right)} \]

energy transferred to R-mode is simultaneously redistributed to TR-modes through the dynamic coupling → have to use \( C^{TR} + C^R \) instead of \( C^R \):

\[ A = \frac{C_i^{HB} \left( C^{TR} + C^R \right)}{C_i^{HB} + \left( C^{TR} + C^R \right)} \frac{1}{\tau} \approx \left( \frac{C^{TR} + C^R}{\tau} \right) \]
\[ C_i^{HB} >> C^{TR} + C^R \]

\( \tau \) – from experimental data
Coarse-graining in modeling of molecular systems

The energy transferred to the dynamic degree of freedom should match the energy lost by the heat bath:

\[ C_i^{HB} \frac{dT_i^{HB}}{dt} = -A(T_i^{HB} - T_i^{R}) \]

\[ \Delta E_i = \Delta E_{HB \rightarrow R} = A(T_i^{HB} - T_i^{R})\Delta t \]

The energy exchange is achieved through an extra “friction” force:

\[ M_i \frac{d^2 R_i}{dt^2} = F_i^{R} + \varepsilon M_i v_i^{R} \]

To change the energy of the dynamic degree of freedom \( R \) of particle \( i \) by \( \Delta E_i \), the expression for \( \varepsilon \) is

\[ \varepsilon = \frac{\Delta E_i}{k_B T_i^{R}} \]


\[ M_i \frac{d^2 R_i}{dt^2} = F_i^{R} + \varepsilon M_i v_i^{R} \]

\[ \varepsilon = \frac{A(T_i^{HB} - T_i^{R})}{k_B T_i^{R}} \]

\[ T_i^{HB} = T_i^{HB} - \Delta E_i / C_i^{HB} \]

these equations ensure the desired energy transfer and energy conservation
## Properties of coarse-grained “water” with local heat bath

Coarse-grained representation of water-like liquid medium


<table>
<thead>
<tr>
<th>properties of water</th>
<th>experiment</th>
<th>CG model</th>
<th>Δ, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>density, $\rho$, g/cm$^3$</td>
<td>1.0</td>
<td>1.0</td>
<td>0</td>
</tr>
<tr>
<td>heat capacity, $c_p$, J/(kg K)</td>
<td>$4.2 \times 10^3$</td>
<td>$4.2 \times 10^3$</td>
<td>0</td>
</tr>
<tr>
<td>bulk modulus, $K$, GPa</td>
<td>2.2</td>
<td>1.8</td>
<td>18</td>
</tr>
<tr>
<td>speed of sound, $c_s$, m/s</td>
<td>1483</td>
<td>1342</td>
<td>9</td>
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<tr>
<td>melting temperature, $T_m$, K</td>
<td>273</td>
<td>330</td>
<td>21</td>
</tr>
<tr>
<td>critical temperature, $T_c$, K</td>
<td>647</td>
<td>520</td>
<td>20</td>
</tr>
<tr>
<td>critical density, $\rho_c$, g/cm$^3$</td>
<td>0.322</td>
<td>0.398</td>
<td>24</td>
</tr>
<tr>
<td>thermal conductivity, $k$, W/(m K)</td>
<td>0.6</td>
<td>0.13</td>
<td>78</td>
</tr>
<tr>
<td>viscosity, $\eta$, cP</td>
<td>0.894</td>
<td>0.910</td>
<td>2</td>
</tr>
<tr>
<td>surface energy, $\sigma$, J/m$^2$</td>
<td>0.072</td>
<td>0.073</td>
<td>1</td>
</tr>
</tbody>
</table>
Coarse grained simulation of laser desorption and deposition of biomolecules

MAPLE technique for “gentle” deposition of thin polymer/biopolymer/nanocomposite films

What is the minimum amount of matrix needed for the ejection of intact polymer molecules?

Laser ablation of lysozyme films with small pockets of water


Desorption & ion separation laser ablation of ionic aqueous protein solutions

Effect of liquid environment on laser processing of metal surfaces

processing of Ag in water
\( \tau_p = 100 \, \text{fs}, \, F_{\text{abs}} = 850 \, \text{J/m}^2 \)

- mechanical confinement → prevents spallation
- additional cooling → strong undercooling & nanocrystallization


single-pulse ablative generation of LIPSS on (001) Cr target

- suppression of the plume expansion
- smoothing of the protrusion before solidification

Shih et al., in preparation
Roughening of water-metal interface due to the Rayleigh-Taylor instability

Rapid deceleration (up to $G = 7 \times 10^{12} \text{ m/s}^2$) of heavier fluid (hot metal layer, $\rho_{ml} = 7 \text{ g/cm}^3$) by lighter fluid (compressed supercritical water $\rho_l = 1.2 \text{ g/cm}^3$) - Rayleigh-Taylor instability at nanoscale!

Fastest growing wavelength: $\lambda_m = 33.9 \text{ nm}$

Characteristic time: $\tau = \left[ \frac{2}{3} \left( \rho_h - \rho_l \right)^{\frac{3}{2}} G^{\frac{3}{2}} \right]^{-\frac{1}{2}}$

$\lambda_m = 33.9 \text{ nm}$ and $\tau = 85 \text{ ps}$ for $G = 1.6 \times 10^{12} \text{ m/s}^2$ at 300 ps

Shih et al., *J. Phys. Chem. C* 121, 16549, 2017; *Nanoscale* 10, 6900, 2018
Laser ablation of bulk Ag in water: nanoparticle generation and quenching

Rapid cooling (~10¹² K/s) of metal droplets injected into cold water region

Quenching & crystallization of liquid droplets within nanoseconds

Generation of unusual defect configurations and metastable phases
Model for laser interaction with metals in liquid environment

\begin{align*}
1 & \quad C_e(T_e) \frac{\partial T_e}{\partial t} = \nabla \cdot \left[ K_e(T_e, T_l) \nabla T_e \right] - G(T_e)(T_e - T_l) + S(\vec{r}, t) \\
2 & \quad C_l(T_l) \frac{\partial T_l}{\partial t} = \nabla \cdot \left[ K_l(T_l) \nabla T_l \right] + G(T_e)(T_e - T_l) \\
3 & \quad m_i \dddot{\vec{r}}_i / \ddt^2 = \vec{F}_i + \zeta m_i \dot{\vec{v}}_i^{th}, \quad \zeta = \frac{1}{n} \sum_{k=1}^{n} GV_N \left( T_e^k - T_l^{cell} \right) / \sum_{cell} \sum_{i} m_i (v_i^{th})^2 \\
4 & \quad \text{pressure-transmitting boundary conditions} \quad T_l^{cell} = \sum_{cell} m_i (v_i^{th})^2 / (3k_B N_{cell}) \\
5 & \quad \text{coarse-grained MD representation of liquid environment}
\end{align*}

The combined TTM-MD model adds **physics missing in classical MD**

- Laser energy absorption by conduction band electrons
- Electron-phonon equilibration
- Electronic heat capacity and heat conduction

“Big picture” of laser ablation from the whole laser spot

“mosaic” approach to mapping the processes occurring at the scale of the whole laser spot


Al target 150 ps after irradiation by a 100 fs pulse

Vorobyev and Guo
*PRB* **72**, 195422, 2005

Ionin et al., JETP Lett. **94**, 753, 2011
Projectile impact on a carbon nanotube film

CNTs are colored by inter-tube interaction energy

V = 100 m/s

Low-velocity impact: Energy spreads over a large area

V = 1000 m/s

High-velocity impact: Energy is localized

How does the energy dissipation into higher-frequency vibrational modes affect:

- Impact resistance of the CNT film
- Final state of the CNT film (damage done by the impact)
Mesoscopic model for carbon nanotube materials

mesoscopic model: nanotubes = chains of stretchable cylindrical segments

Independent dynamic variables (degrees of freedom): \( \mathbf{X} = \left( \mathbf{r}_i^T, \mathbf{r}_k^m, R_i^T, R_k^m, \Theta_i^T \right) \)

Equations of motion: 
\[ M \frac{d^2 \mathbf{X}}{dt^2} = -\frac{\partial U}{\partial \mathbf{X}} + \mathbf{F}_d \]
translational motion
\[ \mathbf{C} \frac{d \mathbf{T}}{dt} = \mathbf{Q}_T + \mathbf{Q}_e + \mathbf{Q}_d \]
internal state of CNTs

\[ \mathbf{U} = \mathbf{U}_{T \text{ (int)}} + \mathbf{U}_{T-T} + \mathbf{U}_{M \text{ (int)}} + \mathbf{U}_{M-M \text{ (non-bonded)}} + \mathbf{U}_{M-T} \]

<table>
<thead>
<tr>
<th>internal CNT modes</th>
<th>CNT-CNT interactions</th>
<th>internal matrix modes</th>
<th>inter-molecular interactions</th>
<th>CNT-matrix interactions</th>
</tr>
</thead>
</table>

References:

* PRB 71, 165417, 2005
* JPC C 114, 5513, 2010
* ACS Nano 4, 6187, 2010
* PRL 104, 215902, 2010
* PRB 86, 165414, 2012
* J. Appl. Phys. 114, 104301, 2013
* Carbon 130, 69, 2018
* Compos. Sci. Technol., in press, 2018
Energy dissipation from low frequency stretching modes in CNTs

Atomistic MD simulations of individual (10,10) CNTs are performed with AIREBO potential. CNTs include fullerene caps and are equilibrated at $T_{init}$ prior to homogeneous stretching/bending.

Results of are reduced to 1D systems by binning unit cells (40 atoms) into nodes

Analysis of energy redistribution in simulations of free stretching and bending vibrations:

- partitioning of the total energy of a CNT into contributions of the longitudinal, bending, radial, and remaining “heat bath” modes
- evaluation of the rates and pathways of the mechanical energy dissipation and redistribution among the vibrational modes.

For CNT composed of 4 260 atoms including two 130-atom caps we have:
99 longitudinal acoustic (LA), 198 bending acoustic (BA), and 900 radial (Rad) modes

Heat Bath: 10 800 modes ($3 \times 4000$ atoms – 99 LA – 198 BA – 900 Rad – 3 translational)

$$E_{HB} = E_{CNT} - (E_{LA} + E_{BA} + E_{Rad})$$

PRB 86, 165414 (2012)
Atomistic MD simulations: Rate of stretching energy dissipation in CNTs

3 regimes:

- **low excitations** (ε < 3.2%)
  - gradual decay of the energy on the time scale of 100s of ps

- **intermediate regime**
  - (3.2% > ε > 4.2%)
  - 2-step process
  - excitation of radial “squash” mode → axial buckling → rapid dissipation

- **strong excitation, ε > 4.2%**
  - immediate transfer of ~90% of the stretching energy
  - axial buckling → rapid dissipation

PRB 86, 165414 (2012)
Atomistic MD simulations: Rate of stretching energy dissipation in CNTs

- Excitation of radial “squash” mode does not reach the critical level.
- Axial buckling → rapid dissipation.
- Axial buckling → immediate dissipation.
Atomistic MD simulations: Rate of **stretching** energy dissipation in CNTs

Rate of energy dissipation from LA modes in stretching I regime ($\varepsilon < 3\%$) as a function of the excess LA energy $E_{LA} - E_{LA}^\theta$ and instantaneous temperature $\theta$.

Data points are obtained by averaging over 10 simulations.

Rate of stretching energy dissipation:

$$
\frac{d}{dt} (E_{LA} - E_{LA}^\theta) = -\gamma^{LA} \left( \frac{E_{LA} - E_{LA}^\theta}{E_{LA}^\theta} \right)^{\alpha^{LA}} (E_{LA}^\theta)^{\beta^{LA}}
$$

$$
\gamma^{LA} = (1.67 \pm 0.41) \times 10^{-3} \text{ eV}^{1-\beta^{LA}} \text{ ps}^{-1}
$$

$$
\alpha^{LA} = 1.34 \pm 0.07
$$

$$
\beta^{LA} = 2.09 \pm 0.10
$$

PRB 86, 165414 (2012)
Atomistic MD simulations: Rate of bending energy dissipation in CNTs

**Regime I: low excitations \((R_c > R^{bcl})\) - slow decay on the timescale of tens of nanoseconds**

**Regime II: high excitations \((R_c < R^{bcl})\) - fast dissipation on the timescale of several periods of bending oscillations**

---

bending buckling  
↓  
rapid dissipation

*PRB 86, 165414 (2012)*
Atomistic MD simulations: Rate of bending energy dissipation in CNTs

Rate of bending energy dissipation:

\[
\frac{d}{dt} (E_{BA} - E_{BA}^\theta) = -\gamma_{BA(I)}^{BA(I)} \left( \frac{E_{BA} - E_{BA}^\theta}{E_{BA}^\theta} \right)^{\alpha_{BA(I)}} \left( E_{BA}^\theta \right)^{\beta_{BA(I)}}
\]

\[-\gamma_{BA(II)}^{BA(II)} \left( \frac{E_{BA} - E_{BA}^\theta}{E_{BA}^\theta} \right)^{\alpha_{BA(II)}} \left( E_{BA}^\theta \right)^{\beta_{BA(II)}} H\left( (E_{BA} - E_{BA}^\theta) - E_{BA}^* \right) \]

\[
\gamma_{BA(I)}^{BA(I)} = (4.58 \pm 0.58) \times 10^{-4} \text{ eV}^{1-\beta_{BA(I)}} \text{ ps}^{-1}
\]

\[
\alpha_{BA(I)}^{BA(I)} = 1.01 \pm 0.07
\]

\[
\beta_{BA(I)}^{BA(I)} = 1.44 \pm 0.06
\]

\[
\gamma_{BA(II)}^{BA(II)} = (4.49 \pm 0.81) \times 10^{-2} \text{ eV}^{1-\beta_{BA(II)}} \text{ ps}^{-1}
\]

\[
\alpha_{BA(II)}^{BA(II)} = 0.94 \pm 0.07
\]

\[
\beta_{BA(II)}^{BA(II)} = 0.84 \pm 0.06
\]

\[
E_{BA}^* = 13.5 \text{ eV} \quad \text{critical excess energy for the onset of buckling}
\]

PRB 86, 165414 (2012)
Mesoscopic description of the energy dissipation

(1) introduction of damping forces
slow energy dissipation (without buckling)

damping force:
\[
\begin{align*}
\vec{F}_d^i &= -\xi_{str} \vec{m}^i \vec{v}_{str}^i - \xi_{bnd} \vec{m}^i \vec{v}_{bnd}^i \\
\vec{v}_{str}^i &= (\vec{v}^i \cdot \vec{e}^i) \vec{e}^i, \quad \vec{v}_{bnd}^i = \vec{v}^i - \vec{v}_{str}^i
\end{align*}
\]

\[\xi_{str} = \frac{\Delta E_{str}}{\Delta t \sum_{i=1}^{N} m^i (\vec{v}_{str}^i)^2} \quad \xi_{bnd} = \frac{\Delta E_{bnd}}{\Delta t \sum_{i=1}^{N} m^i (\vec{v}_{bnd}^i)^2}\]

heat bath temperature increase:
\[\Delta T = \frac{1}{c_{HB}} (\Delta E_{str} + \Delta E_{bnd})\]
\[c_{HB} = 3(n_{at} - N) k_B\]

(2) strain energy hysteresis
fast energy dissipation (with buckling)

bending regime I

bending regime II
Impact resistance of CNT materials

- how is the kinetic energy of the projectile absorbed by CNT material?
- what are the factors that control the penetration depth and energy dissipation?
Simulation of impact resistance and nanoparticle penetration

100-nm-thick film, impact velocity $v_{init} = 1,000$ m/s

- Film: $500 \times 500 \times 100$ nm$^3$, $\rho = 0.2$ g/cm$^3$, 200 nm CNTs
- Projectile: diameter = 50 nm, coarse-grained Pt (20,004 CG units each representing 216 atoms)
Simulation of impact resistance and nanoparticle penetration

100-nm-thick film, impact velocity \( v_{\text{init}} = 1,000 \text{ m/s} \)

CNT internal - degrees of freedom not explicitly present in the mesoscopic model

CNT kinetic - both translational and temperature components

CNT potential - inter-tube interactions, bending and stretching of the CNTs
Simulation of impact resistance and nanoparticle penetration

CNT reorganization is pronounced for slowest loading velocities and should be accounted for in the design of an analytical model for projectile penetration.
Simulation of impact resistance and nanoparticle penetration

300-nm-thick film, impact velocity $v_{\text{init}} = 1,000 \text{ m/s}$

- Film: $500 \times 500 \times 300 \text{ nm}^3$, $\rho = 0.2 \text{ g/cm}^3$, 200 nm CNTs
- Projectile: diameter = 50 nm, coarse-grained Pt (1 CG unit = 216 Pt atoms)
Simulation of impact resistance and nanoparticle penetration

\[ f(E_k) = \frac{dE_k}{dz} \]

\[ E_k = \frac{1}{2}mv^2 \]

\[ z_p = \int_{E_k^{int}}^{0} \frac{1}{f(E_k)} dE_k \]

\( v_i = 1000 \text{ m/s} \)

<table>
<thead>
<tr>
<th>Film Thickness (nm)</th>
<th>-( \Delta v ) (m/s)</th>
<th>Predicted ( \Delta z ) (nm)</th>
<th>% Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>22</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>300</td>
<td>94</td>
<td>448</td>
<td>49</td>
</tr>
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</table>

\( v_i = 500 \text{ m/s} \)

<table>
<thead>
<tr>
<th>Film Thickness (nm)</th>
<th>-( \Delta v ) (m/s)</th>
<th>Predicted ( \Delta z ) (nm)</th>
<th>% Error</th>
</tr>
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<tr>
<td>100</td>
<td>15</td>
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<tr>
<td>300</td>
<td>59</td>
<td>470</td>
<td>57</td>
</tr>
</tbody>
</table>
Simulation of impact resistance and nanoparticle penetration

Entrainment of nanotubes by the projectile results in the enhanced energy deposition to the target and deceleration of the projectile
Mesoscopic simulations of materials far from thermal equilibrium

Computational description of the energy exchange between dynamic degrees of freedom that are represented in coarse-grained mesoscopic model and those that are omitted can enable simulations of non-equilibrium phenomena that involve fast energy deposition from an external source, heat transfer, or dissipation of mechanical energy.