Dissipative Particle Dynamics Simulations with Chemical Reactions: Application to Thermal Decomposition of RDX

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Objective

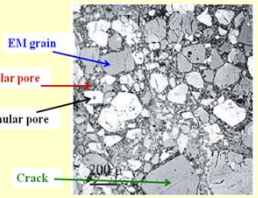
❖ Develop capability to simulate the response of materials to mechanical and thermal stimuli at the micro- and mesoscale[1]

Motivation

➢ Nanocomposites are inherently heterogeneous

➢ Stimuli can incite responses over a wide range of spatial and temporal scales

➢ Known responses include:
- ✓ Structural rearrangements (*e.g.*, plastic deformation)
- ✓ Phase transitions
- ✓ Chemical reactions



Coarse-Grain Models

Top-Down CGing

Build CG model by:

1. Choosing an analytical description of the CG interactions
2. Fitting the CG interaction parameters to observables (experimental or simulation)

[2]**Example: Aluminum**

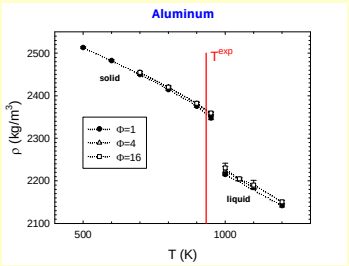
➢ Pair-wise, density-dependent potential[2,3]

$$U_{SC} = \sum_{j>i}\sum \varepsilon_{ij}\left(\frac{r_{0,ij}}{r_{ij}}\right)^{n_{ij}} - \sum C_i \varepsilon_{ii} \sqrt{\sum_{j>i}\left(\frac{r_{0,ij}}{r_{ij}}\right)^{m_{ij}}}$$

long-range, attraction — short-range, cohesion

➢ Fit parameters to 0 K properties (lattice constant, cohesive energy, bulk modulus)

➢ Re-fit to melting temperature using constant-pressure DPD (DPD-P)



Φ: level of coarse-graining

➢ Scale to higher CG levels by fixing:[4]
- number density
- energy per particle

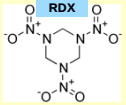
$r_0' = \Phi^{1/3} r_0$

Bottom-Up CGing

Multiscale Coarse-Grain method (MSCG):

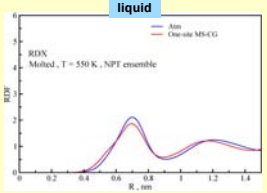
- Force matching approach
- Develop pairwise potentials directly from atomistic simulations

[5]**Example: RDX**

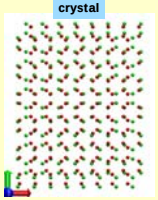


➢ One-site model matched to disordered solid (350 K) and liquid (550 K)

liquid



crystal



centers-of-mass:
atomistic
1-site CG

crystal

Unit cell	Exp.	Atm.	1-site CG
a	13.182	13.4641	12.852
b	11.574	11.5286	12.159
c	10.709	10.5321	10.509
α	90.	90.00	90.2
β	90.	89.98	90.0
γ	90.	89.99	95.1

Methods

Constant-Energy Dissipative Particle Dynamics[6,7] (DPD-E)

➢ Variant of standard Dissipative Particle Dynamics (DPD)

➢ Both momentum and energy conserved in DPD-E

➢ Internal energy variable assigned to each particle, u_i

Equations of motion:

$$\frac{d\mathbf{r}_i}{dt} = \mathbf{v}_i(t) \qquad \textit{position}$$

$$m_i \frac{d\mathbf{v}_i}{dt} = \mathbf{f}_i(t) = \sum_{i\neq j}\left(\mathbf{F}_{ij}^C + \mathbf{F}_{ij}^D + \mathbf{F}_{ij}^R\right) \qquad \textit{velocity}$$

$$\frac{du_i}{dt} = \frac{du_i^{mech}}{dt} + \frac{du_i^{cond}}{dt} \qquad \textit{internal energy}$$

(velocity and internal energy: particles exchange kinetic & internal energy)

- Each particle assigned u_i, s_i and θ_i
- Need *mesoparticle* equation-of-state that governs thermodynamics of implicit d.o.f.
- KE lost/gained by dissipative and random interactions absorbed/released by u_i

Fluctuation-Dissipation Theorems

$$\gamma_{ij} = \frac{\sigma_{ij}^2}{2k_B}\left(\frac{1}{\theta_i} + \frac{1}{\theta_j}\right) \qquad \alpha_{ij}^{\ 2} = 2k_B\kappa_{ij}$$

Mesoparticle EOS: $u_i = u_i(\theta_i)$

Classical Limit: $C_{v,i} = (3n-3)k_B = const$ (n = # of CG DOF)

$$u_i = C_{v,i}\theta_i$$

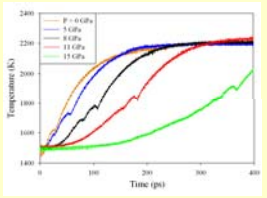
Based on Thermochemical Data:

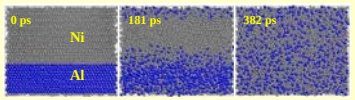
$$u_i = \frac{\Delta H_{f,i}(T_r)}{N_A} + \int_{T_r}^{\theta_i} C_{P,i}^0(T)dT - \frac{5}{2}k\theta_i$$

- **Parameterize $C_v = C_v(\theta)$ data**
- **Possible to include quantum effects from first principles simulation data**

Constant-Enthalpy Dissipative Particle Dynamics[1] (DPD-H)

molecular dynamics simulations of Ni /Al alloying[8]





➢ pressure strongly influences rate of alloying

↓

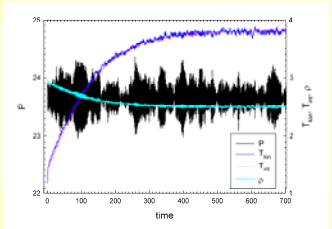
Constant-Enthalpy Method Needed

- Combine DPD-P with DPD-E
- Add either Hoover or Langevin barostat EOM to DPD-E EOM
- Langevin barostat requires "barostat temperature" parameter

Example:

➢ **DPD model fluid**

➢ **1/3 of the particles heated at t=0**



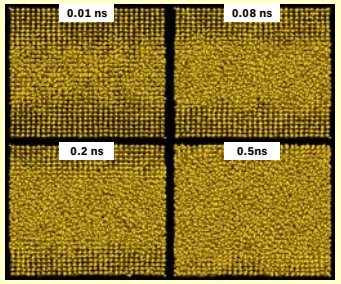
Formulated efficient numerical integration algorithms for DPD varaints[1]

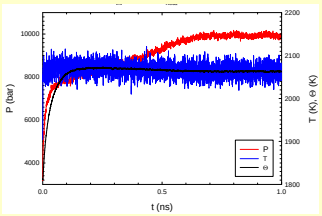
✓required for models of interest ✓improved conservation of quantities

Applications

THERMAL IMPULSE

•CG Ni initially at 1300 K
•interior slab heated to 3000 K

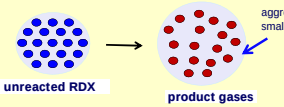




Extension: Chemical Reactions (DPD-RX-E)

- Mesoparticles act as 'microreactors'[9]
- Concentration changes w/i mesoparticles governed by rate eqns.
- Interaction potential depends on concentration: $U_{ij}^C = U_{ij}^C(r_{ij}, [i], [j])$

Ex: RDX decomposition[10]



$$R1: RDX \rightarrow 3CH_2O + 3N_2O$$

$$R2: RDX \rightarrow 3HCN + \frac{3}{2}(NO_2 + NO + H_2O)$$

Rate Equations:

$$\frac{d[RDX]}{dt} = -k_{R1}[RDX] - k_{R2}[RDX]$$

$$\frac{d[CH_2O]}{dt} = 3k_{R1}[RDX]$$

$$\frac{d[NO_2]}{dt} = \frac{3}{2}k_{R2}[RDX]$$

$$\frac{d[N_2O]}{dt} = 3k_{R1}[RDX]$$

$$\frac{d[HCN]}{dt} = 3k_{R2}[RDX]$$

$$\frac{d[NO]}{dt} = \frac{3}{2}k_{R2}[RDX]$$

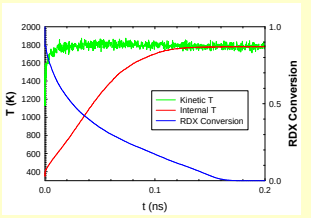
$$\frac{d[H_2O]}{dt} = \frac{3}{2}k_{R2}[RDX]$$

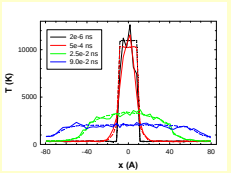
$$k_{Rj} = A_{Rj}\exp\left(-\frac{E_{Rj}}{k_B\theta}\right)$$

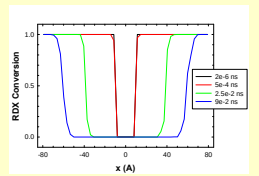
depending on internal temperature

Reaction	A (s^{-1})	E (kJ mol^{-1})
R1	6.02 x 10^{13}	150.624
R2	2.51 x 10^{16}	184.096

Thermal Impulse: pure RDX initially at 350 K ⟹ 20 A slab heated to 10000 K







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