A reduced stochastic model for shock and detonation waves

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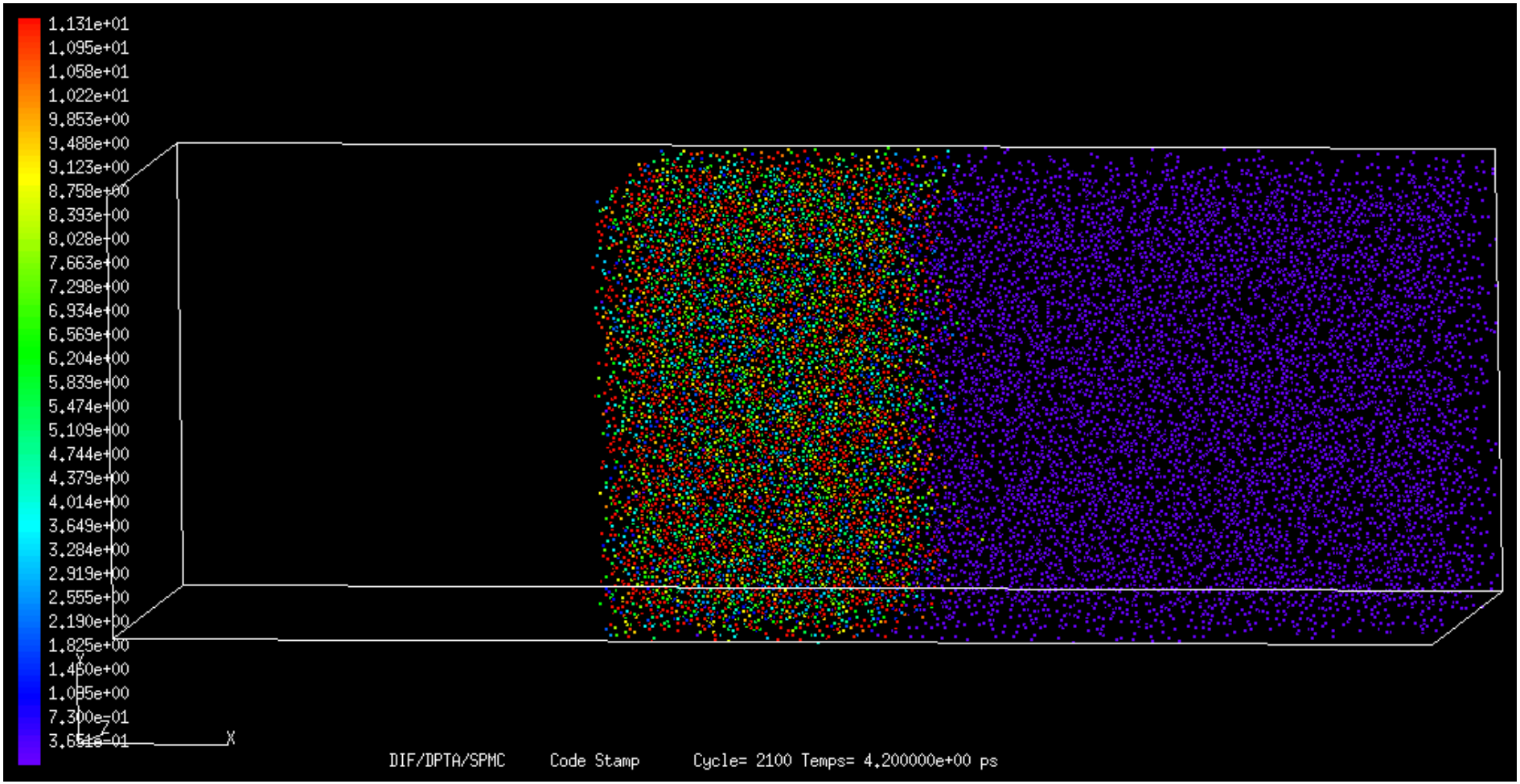
Shock waves: Non equilibrium MD

- (All atom) Hamiltonian dynamics

$$\begin{cases} dq = \quad M^{-1} p \, dt \\ dp = -\nabla V(q) \, dt \end{cases}$$

- Hamiltonian $H(q,p) = \frac{1}{2} p^T M^{-1} p + V(q)$
- All the physics is contained in V!
- Shock obtained through a piston compression
- Bond order potentials such as REBO and ReaxFF are now routinely used and the simulations are qualitatively correct
- Problem = reachable time (ns) and space (μm) scales are not large enough... Ultimately, not all microscopic details are relevant!

A typical simulation



Shock wave in a Lennard-Jones fluid (Hamiltonian dynamics): piston compression + relaxation

Reducing the complexity of the system

- Replace deterministic all atom dynamics by a stochastic dynamics on the variables of interest
- General strategy (Mori-Zwanzig) $\longrightarrow$ average over the unrelevant degrees of freedom to eliminate them: replace their influence by some mean action (drift) and fluctuations around the mean behavior (random noise)
- In this context:
  - 1D model of shock waves in crystalline solids[a]
  - Replace a complex by molecule by a center of mass with some internal energy (unresolved internal modes)[b]

[a] G. Stoltz, *Nonlinearity* **18**, 1967-1985 (2005)

[b] Strachan and Holian, *Phys. Rev. Lett.* (2005)

Reduced dynamics: the inert case

A typical stochastic dynamics

- Langevin dynamics (*e.g.* implicit solvents in biology)

$$\left\{ \begin{array}{l} dq = M^{-1} p \, dt \\ dp = -\nabla V(q) \, dt - \gamma M^{-1} p \, dt + \sigma dW_t \end{array} \right.$$

- Fluctuation/dissipation relation

$$\sigma^2 = 2\gamma k_{\mathrm{B}} \bar{T} = \frac{2\gamma}{\beta}$$

  ensures that the canonical measure is preserved

- Cannot be used for the simulation of shock waves:
  - the dynamics is not invariant through a Galilean transform;
  - the temperature is fixed *a priori*.

(Almost) Dissipative Particle Dynamics

- Galilean invariance $\longrightarrow$ DPD philosophy[a,b]
- Friction depending on the relative velocities (with some cut-off):

$$\begin{cases} dq_i = & \dfrac{p_i}{m_i}\,dt \\ dp_i = & \displaystyle\sum_{j\neq i} -\nabla V(r_{ij})\,dt - \gamma\chi^2(r_{ij})v_{ij}\,dt + \sqrt{\dfrac{2\gamma}{\beta}}\chi(r_{ij})dW_{ij} \end{cases}$$

  - relative distances $r_{ij} = |q_i - q_j|$, relative velocities $v_{ij} = \dfrac{p_i}{m_i} - \dfrac{p_j}{m_j}$
  - (radial) weight function χ with support $[0, r_c]$
  - antisymmetric standard Brownian motions $W_{ij} = -W_{ji}$.
- No projection along the lines of center

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[a] Hoogerbrugge and Koelman, *Europhys. Lett.* **19**(3), 155–160 (1992)

[b] Espanol and Warren, *Europhys. Lett.*, **30**(4), 191–196, (1995)

(Almost) Dissipative Particle Dynamics (2)

- Preserve the canonical measure (cf. Fokker-Planck equation)
- Ergodicity in a 1D framework when density high enough[a]
- Numerical integration through a splitting strategy[b]:
  - Verlet step
  - loop aver particles for a Verlet-like treatment of the dissipation

$$\forall i<j,\ \begin{cases} p_i^{n+1/2} = p_i^n - \frac{1}{2}\gamma\chi^2(r_{ij})v_{ij}^n + \frac{1}{2}\sigma\sqrt{\Delta t}\chi(r_{ij})\,U_{ij}^n, \\ p_j^{n+1/2} = p_j^n + \frac{1}{2}\gamma\chi^2(r_{ij})v_{ij}^n - \frac{1}{2}\sigma\sqrt{\Delta t}\chi(r_{ij})\,U_{ij}^n, \\ p_i^{n+1} = p_i^{n+1/2} - \frac{1}{2}\gamma\chi^2(r_{ij})v_{ij}^{n+1} + \frac{1}{2}\sigma\sqrt{\Delta t}\chi(r_{ij})\,U_{ij}^n, \\ p_j^{n+1} = p_j^{n+1/2} + \frac{1}{2}\gamma\chi^2(r_{ij})v_{ij}^{n+1} - \frac{1}{2}\sigma\sqrt{\Delta t}\chi(r_{ij})\,U_{ij}^n, \end{cases}$$

[a] Shardlow and Yan, *Stochastics and dynamics* **6**(1) (2006)

[b] T. Shardlow, *SIAM J. Sci. Comput.* **24**(4) (2003) 1267-1282

Dissipative Particle Dynamics with conserved energy (DPDE)

- Variation of temperature when the shock passes? Energy conservation: transfers between external and internal modes (DPDE[a,b] philosophy)
- Replace a complex by molecule by[c]
  - a center of mass, effective interactions $H(q,p)$
  - an internal energy ϵ = all the unresolved (internal) modes
- Evolution such that $dH(q,p) + \sum_i d\epsilon_i = 0$
- Microscopic state law: entropy $s = s(\epsilon)$, internal temperature defined from the entropy as $T_i = \left(\frac{\partial s_i}{\partial \epsilon_i}\right)^{-1}$
- Harmonic internal degrees of freedom: $T(\epsilon) = \frac{\epsilon}{C_v}$

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[a] Avalos and Mackie, *Europhys. Lett.* **40**, 141-146 (1997)

[b] Español, *Europhys. Lett.* **40** 631-636 (1997)

[c] Strachan and Holian, *Phys. Rev. Lett.* (2005)

Dissipative Particle Dynamics with conserved energy (2)

- Store energy dissipated by the frictional forces in the internal energies

$$\begin{cases} dq_i = & \dfrac{p_i}{m_i}\,dt \\ dp_i = & \displaystyle\sum_{j,\,j\neq i} -\nabla V(r_{ij})\,dt - \gamma_{ij}\chi^2(r_{ij})v_{ij}\,dt + \sigma_{ij}\chi(r_{ij})dW_{ij}, \\ d\epsilon_i = & \dfrac{1}{2}\displaystyle\sum_{j,\,j\neq i}\left(\chi^2(r_{ij})\gamma_{ij}v_{ij}^2 - \frac{\sigma_{ij}^2}{2}\left(\frac{1}{m_i}+\frac{1}{m_j}\right)\chi^2(r_{ij})\right)dt \\ & \qquad -\sigma_{ij}\,\chi(r_{ij})v_{ij}\cdot dW_{ij}, \end{cases}$$

- Fluctuation-dissipation relation depending on the internal temperatures:

  $\sigma_{ij} = \sigma^2$ and $\gamma_{ij} = \dfrac{\sigma^2}{\beta_{ij}}$ with $\beta_{ij} = \dfrac{1}{2k_{\mathrm{B}}}\left(\dfrac{1}{T_i}+\dfrac{1}{T_j}\right)$ to preserve the measure

$$d\mu(q,p,\epsilon) = \frac{1}{Z}\mathrm{e}^{-\beta(H(q,p)+f(\epsilon))}\,dq\,dp\,d\epsilon$$

  where $f(\epsilon) = \epsilon - \bar{T}s(\epsilon)$ is a free energy

Numerical implementation

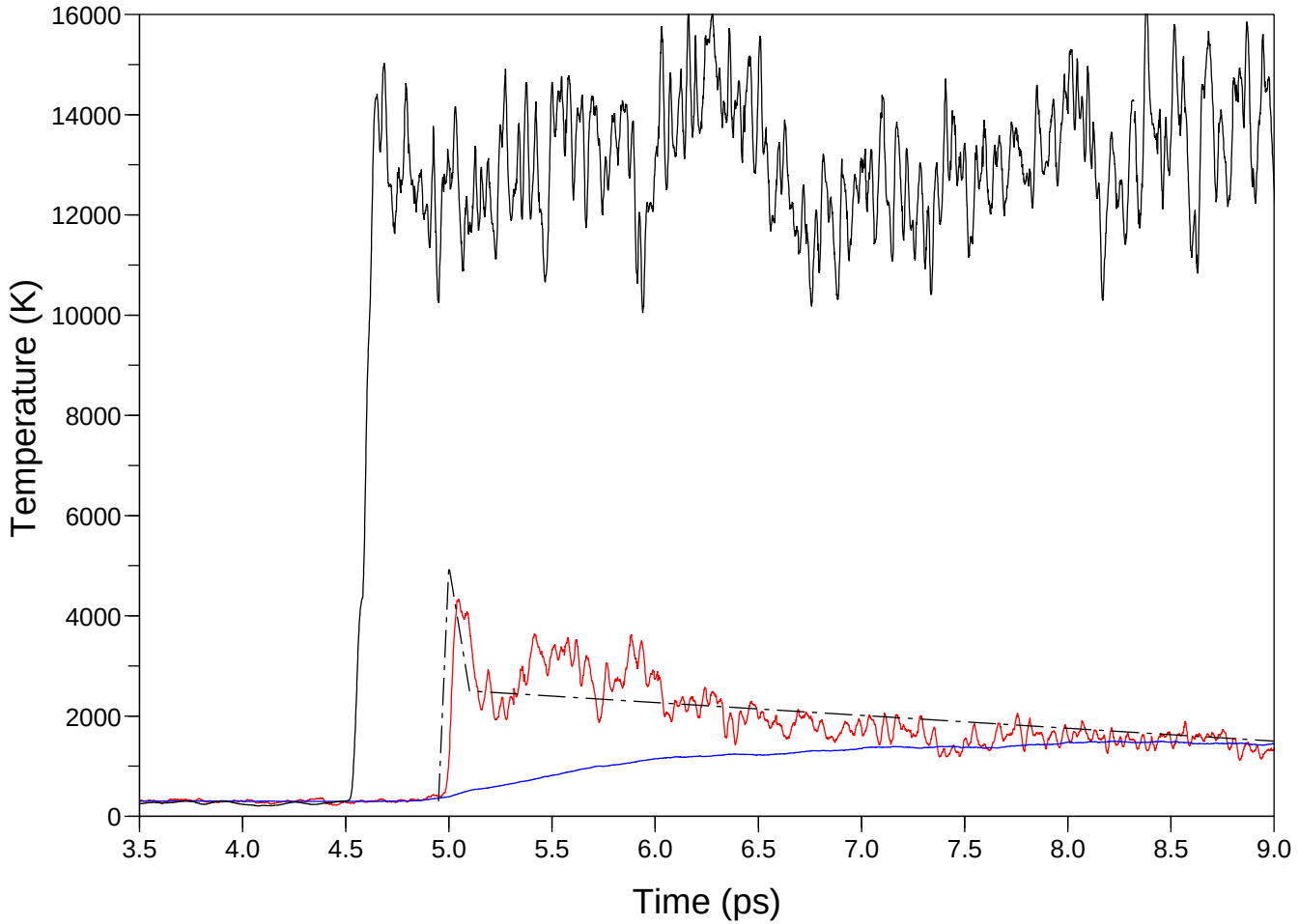
- Existence of invariants: total energy and total momentum
- Numerical scheme based on splitting
  - Hamiltonian part $\left\{ \begin{array}{ll} dq = & M^{-1} p \, dt, \\ dp = & -\nabla V(q) \, dt \end{array} \right.$, velocity Verlet scheme
  - stochastic part:

$$\forall i < j, \quad \left\{ \begin{array}{ll} dp_i = & -\gamma_{ij} \chi^2(r_{ij}) v_{ij} \, dt + \sigma \chi(r_{ij}) \, dW_{ij}, \\ dp_j = & -dp_i, \\ d\epsilon_i = & -\frac{1}{2} d \left(\frac{p_i^2}{2m_i} + \frac{p_j^2}{2m_j} \right), \\ d\epsilon_j = & d\epsilon_i. \end{array} \right.$$

- Estimators of the thermodynamic temperature

$$k_{\mathrm{B}} \langle T_{\mathrm{kin}} \rangle = \beta^{-1}, \quad k_{\mathrm{B}} \left(\left\langle \frac{1}{T_{\mathrm{int}}} \right\rangle \right)^{-1} = \beta^{-1}$$

An example (PVDF)



Average temperature in a slice: $\hat{T}_{\mathrm{kin}}$, $\hat{T}_{\mathrm{int}}$, compared with $\hat{T}_{\mathrm{kin}}$ when $C_v = 0$.

Reduction: from 18 d.d.l. to 3, time step $\Delta t = 10^{-14}$ s !

Reduced dynamics: the reactive case

The progress variable

- One more parameter per particle: progress variable λ_i, describing the progress along the free energy profile associated with the decomposition process
- The interaction potential depends on the reaction rate. For instance, in the Lennard-Jones case,

$$V_{ij}(r_{ij}, \lambda_i, \lambda_j) = 4E_{ij}\left(\left(\frac{a_{ij}}{r_{ij}}\right)^{12} - \left(\frac{a_{ij}}{r_{ij}}\right)^{6}\right),$$

  with $E_{ij} = E\sqrt{(1 + k_E\lambda_i)(1 + k_E\lambda_j)}$, $a_{ij} = a\,(1 + k_a(\lambda_i + \lambda_j)/2)$.
- Reversible kinetics AB $\rightleftarrows$ A_2 + B_2, depending on the temperature

$$\frac{d\lambda_i}{dt} = \sum_{i \neq j} \omega(r_{ij})\left[K_1(T_{ij}^{\text{int}})(1 - \lambda_j)(1 - \lambda_i) - K_2(T_{ij}^{\text{int}})\lambda_j\lambda_i\right]$$

- For instance, arrhénius form $K_i(T) = Z_i \mathrm{e}^{-E_i/k_{\mathrm{B}}T}$.

Treating the exothermicity

- Exothermicity of the reaction $\Delta E_{\text{exthm}} (= E_2 - E_1)$.
- Seek a dynamics such that $dH_{\text{tot}}(q, p, \epsilon, \lambda) = 0$ with

$$dH_{\text{tot}}(q, p, \epsilon, \lambda) = d \left[\sum_{1 \leq i < j \leq N} V(r_{ij}, \lambda_i, \lambda_j) + \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \epsilon_i + (1 - \lambda_i) \Delta E_{\text{exthm}} \right].$$

- Additional assumption: during the elementary step corresponding to exothermicity, the total energy of a given mesoparticle does not change:

$$d \left[\frac{1}{2} \sum_{i \neq j} V(r_{ij}, \lambda_i, \lambda_j) \right] + d \left(\frac{p_i^2}{2m_i} \right) + d\epsilon_i - \Delta E_{\text{exthm}} d\lambda_i = 0.$$

- Evolutions of momenta and internal energies balancing the variations in the total energy due to the variations of λ (exothermicity, changes in the potential energies) $\rightarrow$ processes Z_i^p, Z_i^ϵ.

Treating the exothermicity (2)

- Distribution between internal energies and kinetic energies following some predetermined ratio $0 < c < 1$.
- For the internal energies (fix r, vary λ)

$$d\epsilon_i = -c \left(d \left[\frac{1}{2} \sum_{i \neq j} V(r_{ij}, \lambda_i, \lambda_j) \right] - \Delta E_{\text{exthm}} d\lambda_i \right).$$

- For the momenta, we consider a process Z_i^p such that $dp_i = dZ_i^p$ with

$$d\left(\frac{p_i^2}{2m}\right) = -(1-c) \left(d \left[\frac{1}{2} \sum_{i \neq j} V(r_{ij}, \lambda_i, \lambda_j) \right] - \Delta E_{\text{exthm}} d\lambda_i \right).$$

In practice (2D case), for a variation δE_i^n due to the variations of $\{\lambda_i^n\}$,

$$p_i^{n+1} = p_i^n + \alpha^n(\cos\theta^n, \sin\theta^n), \qquad \frac{(p_i^{n+1})^2}{2m_i} = \frac{(\tilde{p}_i^n)^2}{2m_i} + (1-c)\,\delta E_i^n.$$

The reactive DPDE dynamics

- Finally, the reactive DPDE dynamics is

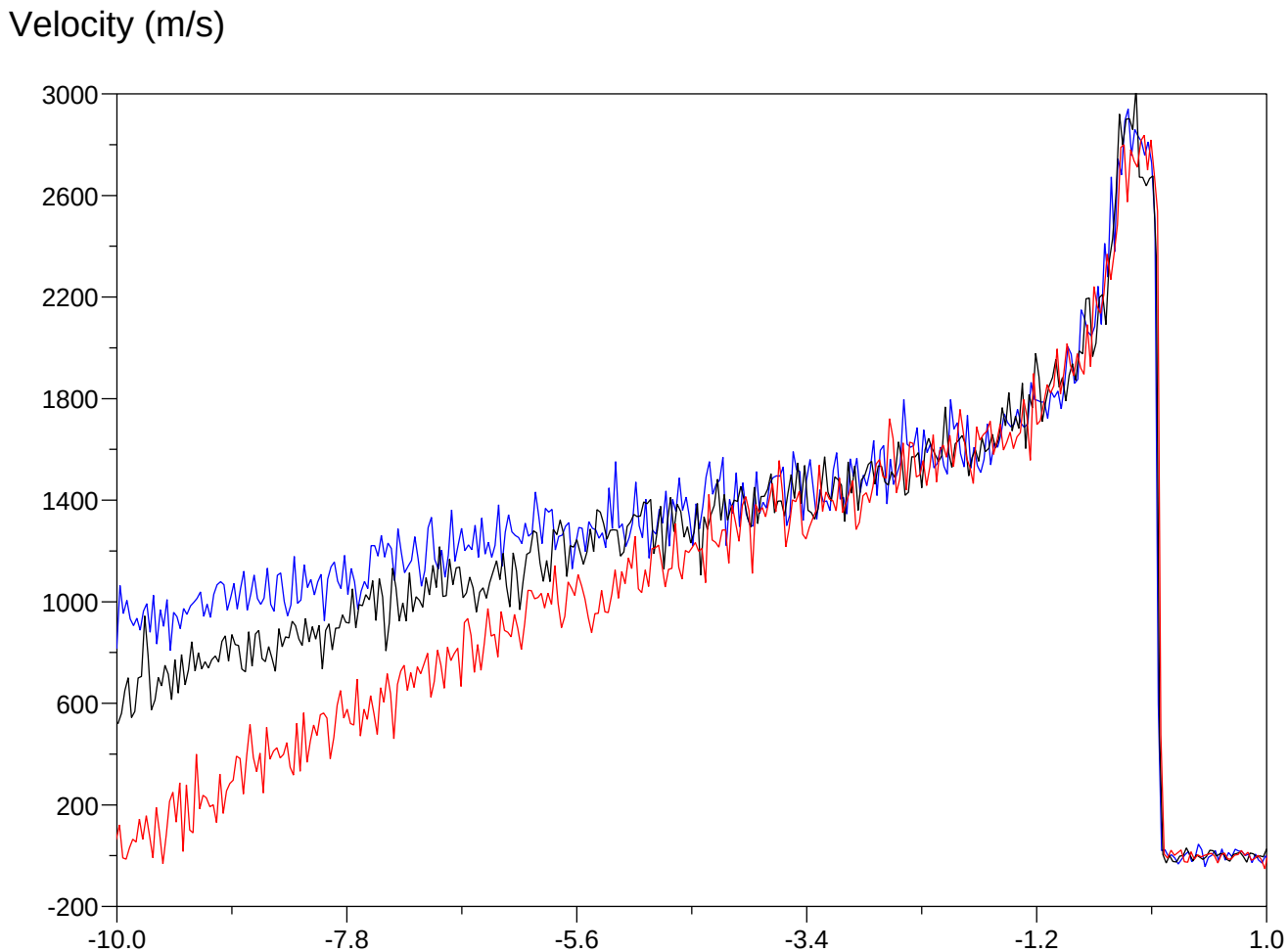
$$
\begin{aligned}
dq_i &= \frac{p_i}{m_i}\,dt, \\
dp_i &= \sum_{j,\,j\neq i} -\nabla_{q_i} V(r_{ij},\lambda_i,\lambda_j)\,dt - \gamma_{ij}\chi^2(r_{ij})v_{ij}\,dt + \sigma\chi(r_{ij})dW_{ij} + dZ_i^p, \\
d\epsilon_i &= \frac{1}{2}\sum_{j,\,j\neq i}\left(\chi^2(r_{ij})\gamma_{ij}v_{ij}^2 - \frac{d\sigma^2}{2}\left(\frac{1}{m_i}+\frac{1}{m_j}\right)\chi^2(r_{ij})\right)dt \\
&\qquad -\sigma\,\chi(r_{ij})v_{ij}\cdot dW_{ij} + dZ_i^\epsilon, \\
d\lambda_i &= \sum_{j\neq i}\omega_r(r_{ij})\left[K_1(T_{ij})(1-\lambda_i)(1-\lambda_j) + K_2(T_{ij})\lambda_i\lambda_j\right]\,dt,
\end{aligned}
$$

- Numerical implementation: splitting of the dynamics as (inert) + (reaction)
- Integration of the reaction: update first λ_i, compute then the exothermicity (variations in the potential and liberated chemical energy), compute finally the new internal energies and velocities.

Numerical application

- Parameters inspired by the nitromethane example (replace CH_3NO_2 by a mesoparticle in a space of 2 dimensions).
- Classification of the parameters in five main categories
  - (Material parameters) molar mass $m = 80$ g/mol, Lennard-Jones potential with $E_{\mathrm{LJ}} = 3 \times 10^{-21}$ J (melting 220 K), $a = 5$ Å, cut-off radius $r_{\mathrm{cut}} = 15$ Å for the computation of forces. Changes of the material use $k_E = 0$ and $k_a = 0.2$ (pure expansion).
  - (Parameters of the inert dynamics) Microscopic state law is $\epsilon = C_v T$ with $C_v = 10\ k_{\mathrm{B}}$ (*i.e.*, 20 d.o.f). Friction is $\gamma = 10^{-15}$ kg/s, dissipation weighting function $\chi(r) = (1 - r/r_{\mathrm{c}})$, with $r_{\mathrm{c}} = r_{\mathrm{cut}}$.
  - (Chemical kinetics) Prefactors $Z_1 = Z_2 = 10^{17}$ s^{-1}, activation energies $E_1/k_{\mathrm{B}} = 15000$ K, exothermicity $\Delta E_{\mathrm{exthm}} = 6.25$ eV. Weighting function $\omega(r) = \chi(r)$;
  - (Exothermicity) distribution fraction $c = 0.5$.
  - (Initial conditions) density $\rho = 1.06$ g/cm^3, temperature $\bar{T} = 300$ K.

Numerical application (2)



Velocity profiles in the material at different times (lower curve (red): $t = 1.2 \times 10^{-10}$ s; middle curve (black): $t = 1.6 \times 10^{-10}$ s; upper curve (blue): $t = 2 \times 10^{-10}$ s). Time-step $\Delta t = 2 \times 10^{-15}$ s.

Conclusion and perspectives

- Systematic parametrization from small all atom simulations (potential, friction, microscopic state law $s = s(\epsilon)$, reaction constants, exothermicity)
- Dimensionality reduction allows to treat larger systems, for longer times $\rightarrow$ truly mesoscopic model? (polycrystalline materials)
- Hierarchy of models from discrete to continuum hydrodynamic equations (discretized with particle methods such as *Smoothed Particle Hydrodynamics*)
- References for this work:
  - G. STOLTZ, A reduced model for shock and detonation waves. I. The inert case, *Europhys. Lett.* **76**(5) (2006) 849-855.
  - J.-B. MAILLET, L. SOULARD AND G. STOLTZ, A reduced model for shock and detonation waves. II. The reactive case, accepted for publication in *Europhys. Lett.* (2007).