European Research Council

Established by the European Commission

Parametrizing coarse-grained molecular systems from ab-initio computations: some elements

Gabriel STOLTZ

gabriel.stoltz@enpc.fr

(CERMICS, Ecole des Ponts & MATHERIALS team, INRIA Paris)

Work also supported by ANR Funding ANR-14-CE23-0012 ("COSMOS")

IPAM, L.A., October 2016

Outline

- Dissipative Particle Dynamics (Isothermal)
- Dissipative Particle Dynamics with energy conservation
- Parametrizing DPDE
- Some numerical results: shock waves in molecular systems
- Coarse-graining even further: SDPD[1]

[1] depending on the remaining time...

Dissipative Particle Dynamics

Langevin dynamics

- Positions $q = (q_1, \ldots, q_N) \in \mathcal{D}$ and momenta $p = (p_1, \ldots, p_N) \in \mathbb{R}^{dN}$
- Hamiltonian $H(q,p) = V(q) + \frac{1}{2} p^T M^{-1} p$

Stochastic perturbation of the Hamiltonian dynamics

$$\begin{cases} dq_t = M^{-1} p_t \, dt \\ \\ dp_t = -\nabla V(q_t) \, dt - \gamma M^{-1} p_t \, dt + \sqrt{\dfrac{2\gamma}{\beta}} \, dW_t \end{cases}$$

- Friction $\gamma > 0$ (could be a position-dependent matrix)
- Existence and uniqueness of the invariant measure (canonical measure)

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

- Various ergodicity results (including exponential convergence of the law)[2]

[2] T. Lelièvre and G. Stoltz, *Acta Numerica* (2016)

Dissipative Particle Dynamics (1)

- Langevin dynamics not Galilean invariant, hence not consistent with hydrodynamics $\rightarrow$ friction forces depending on relative velocities[3]

Dissipative Particle Dynamics

$$\begin{cases} dq_t = M^{-1} p_t \, dt \\ dp_{i,t} = -\nabla_{q_i} V(q_t) \, dt + \sum_{i \neq j} \left(-\gamma \chi^2(r_{ij,t}) v_{ij,t} \, dt + \sqrt{\frac{2\gamma}{\beta}} \chi(r_{ij,t}) \, dW_{ij} \right) \end{cases}$$

with $r_{ij} = |q_i - q_j|$ and $v_{ij} = \frac{p_i}{m_i} - \frac{p_j}{m_j}$

- Antisymmetric stochastic forcing: $W_{ij} = -W_{ji}$
- Cut-off function χ for the interaction, *e.g.* $\chi(r) = \left(1 - \frac{r}{r_{\text{cut}}}\right) 1_{r \leqslant r_{\text{cut}}}$

[3] P. J. Hoogerbrugge and J. M. V. A. Koelman, *Europhys. Lett.* (1992)

Dissipative Particle Dynamics (2)

- Can be generalized to anisotropic frictions, *e.g.* only along $e_{ij} = \dfrac{r_{ij}}{|r_{ij}|}$
- Generator $\mathcal{L} = \mathcal{L}_{\mathrm{ham}} + \gamma \sum_{1 \leqslant i < j \leqslant N} \mathcal{L}_{\mathrm{FD},ij}$ with

$$\mathcal{L}_{\mathrm{FD},ij} = \chi^2(r_{ij}) \left(-v_{ij} \cdot (\nabla_{p_i} - \nabla_{p_j}) + \frac{1}{\beta} (\nabla_{p_1} - \nabla_{p_2})^2 \right)$$

- Thermodynamic consistency[4]

Invariant measure

$$\mu_{\mathrm{DPD}}(dq\, dp) = Z^{-1} \mathrm{e}^{-\beta H(q,p)} \delta_{\left\{\sum_{i=1}^N p_i - P_0\right\}}(dp)\, dq$$

- Ergodicity is an issue $\rightarrow$ proved for $d = 1$ only[5]

[4] P. Espanol and P. Warren, *Europhys. Lett.* (1995)
[5] T. Shardlow and Y. Yan, *Stoch. Dynam.* (2006)

Dissipative Particle Dynamics: numerical schemes

- Many schemes, often dubious extensions of Verlet-like/BBK schemes
- More appropriate alternatives: splitting schemes[6][7]
- My favorite one:
  - Verlet step to update (q, p)
  - For each pair of particles, analytically integrate the elementary fluctuation/dissipation dynamics $\mathcal{L}_{\mathrm{FD},ij}$

$$dv_{ij} = -\gamma \left(\frac{1}{m_i} + \frac{1}{m_j} \right) \chi^2(r_{ij,t}) v_{ij,t}\, dt + \sqrt{\frac{2\gamma}{\beta}} \left(\frac{1}{m_i} + \frac{1}{m_j} \right) \chi(r_{ij,t})\, dW_{ij}$$

[6] T. Shardlow, *SIAM J. Sci. Comput.* (2003)
[7] B. Leimkuhler and X. Shang, J. Comput. Phys. (2015)

Dissipative Particle Dynamics with energy preservation

Construction of the dynamics: a simplified case (1)

- Enforcing energy conservation in the Langevin dynamics?

$\rightarrow$ Gather energy variation in some additional variable $\varepsilon \in \mathbb{R}_+$

$$d\varepsilon_t = -d\Big(H(q_t, p_t)\Big) = \left(\gamma \frac{p_t^2}{m} - \frac{\sigma^2}{2m}\right) dt - \sigma \frac{p_t}{m} \cdot dW_t$$

- The variable ε can be interpreted as some coarse-grained internal energy

$\rightarrow$ entropy $s(\varepsilon)$

$$\begin{cases} dq_t = \dfrac{p_t}{m}\, dt \\ dp_t = -\nabla V(q_t)\, dt - \gamma \dfrac{p_t}{m}\, dt + \sqrt{\dfrac{2\gamma}{\beta}}\, dW_t, \\ d\varepsilon_t = \left(\gamma \dfrac{p_t^2}{m} - \dfrac{\sigma^2}{2m}\right) dt - \sigma \dfrac{p_t}{m} \cdot dW_t. \end{cases}$$

- Generator $\mathcal{L}_{\mathrm{ham}} + \mathcal{L}_{\mathrm{FD}}$ with $\mathcal{L}_{\mathrm{FD}} = -\gamma \dfrac{p}{m} \cdot \mathcal{A} + \dfrac{\sigma^2}{2} \mathcal{A}^2$ and $\mathcal{A} = \nabla_p - \dfrac{p}{m} \partial_\varepsilon$

Construction of the dynamics: a simplified case (2)

- Invariance of measures of the form (mind the factor $\mathrm{e}^{s(\varepsilon)}$...)

$$\rho(dq\,dp\,d\varepsilon) = f\Big(H(q,p)+\varepsilon\Big)\,\mathrm{e}^{s(\varepsilon)}\,dq\,dp\,d\varepsilon$$

- Sufficient condition $\mathcal{L}_{\mathrm{FD}}^{\dagger}\rho = 0$, *i.e.* $\gamma\dfrac{p}{m}\rho + \mathcal{A}\left(\dfrac{\sigma^2}{2}\rho\right) = 0$

- Possible choice: $\gamma = \gamma(\varepsilon)$ and $\sigma \in \mathbb{R}$

Fluctuation/dissipation relation

$$\sigma^2 = \frac{2\gamma}{s'(\varepsilon)}$$

- $T(\varepsilon) = \dfrac{1}{s'(\varepsilon)}$ interpreted as some internal temperature

DPDE for many-particle systems (1)

- Coarse-graining interpretation:
  - a (fragment of a) molecule is replaced by a mesoparticle
  - (q_i, p_i) describes the center of mass of the ith mesoparticle
  - missing degrees of freedom described by an internal energy ε_i

- Evolution at constant total energy $\mathcal{H}(q,p,\varepsilon) = V(q) + \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + \sum_{i=1}^{N} \varepsilon_i$

- Microscopic state law: entropies $s_i = s_i(\varepsilon_i)$, internal temperature defined from the entropy as

$$T_i(\varepsilon_i) = \frac{1}{s_i'(\varepsilon_i)}$$

- Simplest case: harmonic internal degrees of freedom, $T(\varepsilon) = \varepsilon / C_v$

J. Bonet Avalos and A. Mackie, *Europhys. Lett.* **40**, 141-146 (1997)
P. Español, *Europhys. Lett.* **40** 631-636 (1997)

DPDE for many-particle systems (2)

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

Invariant measures

$$\rho(dq\, dp\, d\varepsilon) = f\Big(\mathcal{H}(q,p,\varepsilon)\Big) g\left(\sum_{i=1}^N p_i\right) \exp\left(\sum_{i=1}^N s_i(\varepsilon_i)\right) dq\, dp\, d\varepsilon,$$

- Fluctuation-dissipation relation

$$\sigma_{ij} = \sigma, \quad \gamma_{ij} = \frac{\sigma^2 \beta_{ij}(\varepsilon_i, \varepsilon_j)}{2}, \quad \beta_{ij}(\varepsilon_i, \varepsilon_j) = \frac{1}{2k_{\mathrm{B}}} \left(\frac{1}{T_i(\varepsilon_i)} + \frac{1}{T_j(\varepsilon_j)} \right)$$

Thermodynamic properties

• In favorable situations (...) the dynamics should be ergodic with respect to the measure

$$\rho_{E_0,P_0} = Z^{-1}_{E_0,P_0} \delta_{\{\mathcal{H}(q,p,\varepsilon)-E_0\}} \delta_{\left\{\sum_{i=1}^N p_i - P_0\right\}} \exp\left(\sum_{i=1}^N s_i(\varepsilon_i)\right)$$

• When $P_0 = 0$, this measure is equivalent in the thermodynamic limit to the canonical measure

$$\rho_\beta(dq\, dp\, d\varepsilon) = Z_\beta^{-1} \mathrm{e}^{-\beta H(q,p)} \prod_{i=1}^N \mathrm{e}^{-\beta f_i(\varepsilon_i)}\, dq\, dp\, d\varepsilon$$

where $f_i(\varepsilon_i) = \varepsilon_i - \dfrac{s_i(\varepsilon_i)}{\beta}$ is a free energy and β is such that $\mathbb{E}_{\rho_\beta}(\mathcal{H}) = E_0$

• Estimators of the temperature

$$T_{\mathrm{kin}}(p) = \frac{1}{dNk_{\mathrm{B}}} \sum_{i=1}^N \frac{p_i^2}{m_i}, \qquad T_{\mathrm{int}}(\varepsilon) = \left(\frac{1}{N}\sum_{i=1}^N \frac{1}{T_i(\varepsilon_i)}\right)^{-1}$$

Adding thermal conduction

- Additional elementary pairwise fluctuation/dissipation dynamics

$$\begin{cases} d\varepsilon_i = \kappa\chi^2(r_{ij}) \left(\dfrac{1}{T_i(\varepsilon_i)} - \dfrac{1}{T_j(\varepsilon_j)} \right) dt + \sqrt{2\kappa}\chi(r_{ij})\, d\widetilde{W}_{ij}, \\ d\varepsilon_j = -d\varepsilon_i, \end{cases}$$

where $\kappa > 0$ is a thermal conductivity

- This dynamis preserves
  - the elementary energy $\varepsilon_i + \varepsilon_j$ by construction
  - measures of the form $f(\varepsilon_i + \varepsilon_j)\, \mathrm{e}^{s_i(\varepsilon_i)+s_j(\varepsilon_j)}\, d\varepsilon_i\, d\varepsilon_j$

- Static thermodynamic properties therefore unchanged

Numerical integration of DPDE (1)

- Splitting strategy: Hamiltonian part and elementary dynamics

$$\begin{cases} dp_i = -\gamma(\varepsilon_i, \varepsilon_j)\chi^2(r_{ij})v_{ij}\,dt + \sigma\chi(r_{ij})\,dW_{ij}, \\ dp_j = -dp_i, \\ d\varepsilon_i = \dfrac{\chi^2(r_{ij})}{2}\left[\gamma(\varepsilon_i, \varepsilon_j)v_{ij}^2 - \dfrac{\sigma^2}{2}\left(\dfrac{1}{m_i} + \dfrac{1}{m_j}\right)\right]dt - \dfrac{\sigma}{2}\chi(r_{ij})v_{ij}\cdot dW_{ij}, \\ d\varepsilon_j = d\varepsilon_i, \end{cases}$$

- In fact, can be reduced to a dynamics on v_{ij} only

$$dv_{ij} = -\gamma(\varepsilon_i, \varepsilon_j)\chi^2(r_{ij})\left(\frac{1}{m_i} + \frac{1}{m_j}\right)v_{ij}\,dt + \sigma\chi(r_{ij})\left(\frac{1}{m_i} + \frac{1}{m_j}\right)dW_{ij}$$

since, by the energy conservation (recall $p_i + p_j$ is constant),

$$\varepsilon_i = \varepsilon_{i,0} + \frac{1}{2}\left(\frac{p_i^2 - p_{i,0}^2}{2m_i} + \frac{p_j^2 - p_{j,0}^2}{2m_j}\right) = \varepsilon_{i,0} + F(v_{ij}), \qquad \varepsilon_j = \varepsilon_{j,0} + F(v_{ij})$$

Numerical integration of DPDE (2)

- **Practical integrator:**
  - integrate the dynamics on v_{ij} with fixed friction
  - update the internal energies to ensure the energy conservation
  - it is possible to superimpose a Metropolis correction[8] [w.r.t. some locally invariant measure]

- **Pro/cons of this integrator:**
  - automatically corrects for negative internal energies (stabilization)
  - parallelization/threadability limited $\rightarrow$ dedicated schemes for that[9]

[8] G. Stoltz, in preparation

[9] A.-A. Homman, J.-B. Maillet, J. Roussel and G. Stoltz, *J. Chem. Phys* (2016)

Parametrization of DPDE

Summary of the quantities to provide

- **Static properties**
  - effective masses for mesoparticles
  - microscopic state law $\varepsilon = \int_0^{T(\varepsilon)} C_v(\theta)\, d\theta$
  - effective interaction potential $\rightarrow$ machine learning approaches[10]
- **Dynamical properties**
  - fluctuation magnitude σ
  - thermal conductivity κ
  - cut-off functions for the fluctuation/dissipation dynamics
- **Derivation of DPDE?** From Hamiltonian dynamics[11]

[10] G. Ferré, J.-B. Maillet and G. Stoltz, *J. Chem. Phys.* (2015)
[11] P. Español, M. Serrano, I. Pagonabarraga and I. Zúñiga, *Soft Matter* (2016)

Estimating some of the quantities

- **Microscopic state law**: energy as a function of the temperature
  - ab-initio computations of the rovibrational modes
  - integration using some distribution function (Bose–Einstein)
  - invert to obtain the temperature as a function of the energy

- **Fluctuation magnitude**: equilibration dynamics[12]
  - initialize internal and external degrees of freedom at different temperatures

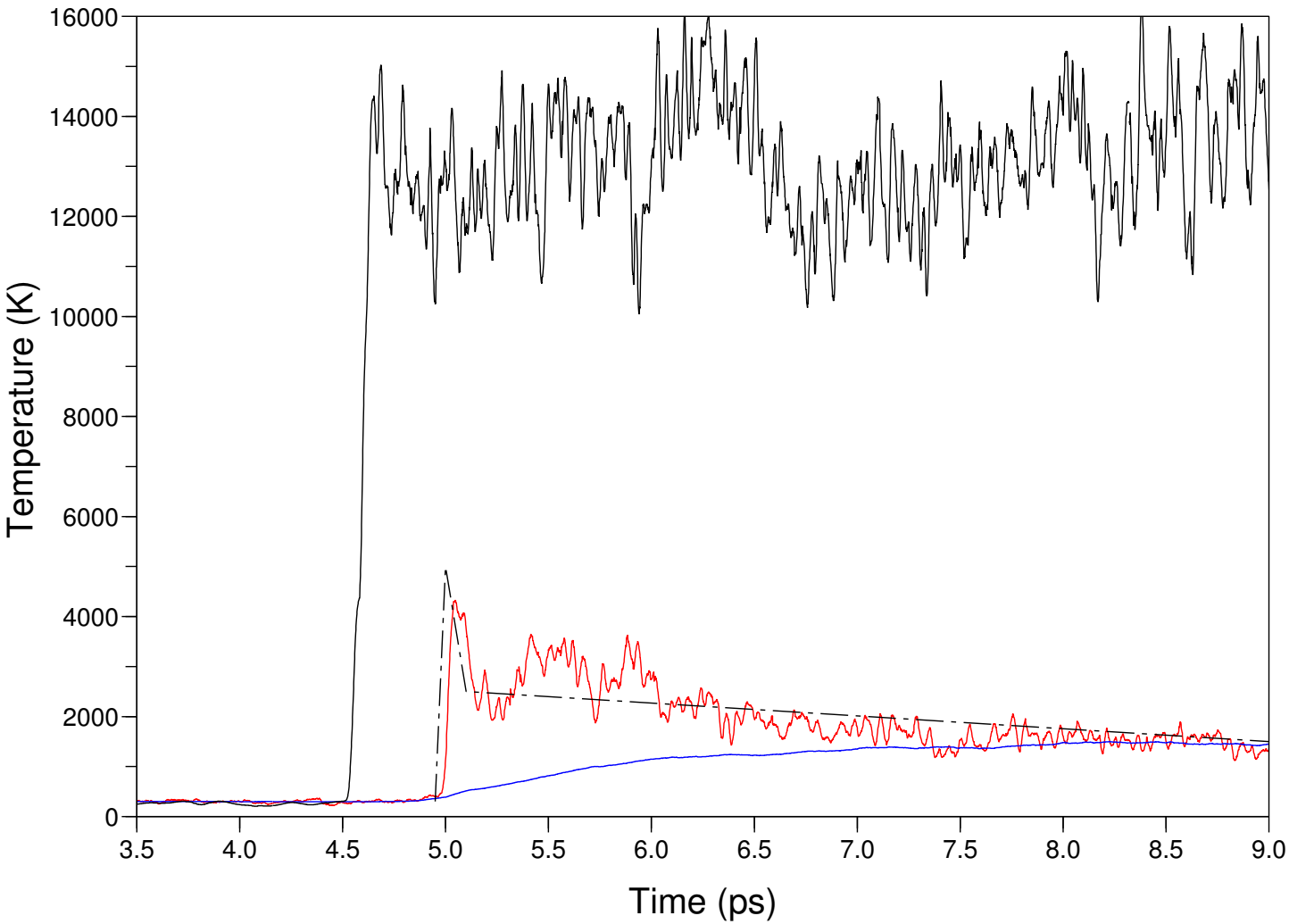
$$\rho_{\beta_{\mathrm{ext}},\beta_{\mathrm{int}}}(dq\,dp\,d\varepsilon) = Z_\beta^{-1} \mathrm{e}^{-\beta_{\mathrm{ext}} H(q,p)} \prod_{i=1}^{N} \mathrm{e}^{-\beta_{\mathrm{int}} f_i(\varepsilon_i)}\, dq\,dp\,d\varepsilon$$

  - compute the time evolution of internal and external (kinetic) temperatures $\rightarrow$ timescale for return to equilibrium
  - reference all-atom simulation (small system)

[12] M. Kroonblawd, T. Sewell and J.-B. Maillet, *J. Chem. Phys.* (2016)

Some numerical results

Shock waves in an effective material



G. Stoltz, *Europhys. Lett.* (2006)

Detonation waves in nitromethane (1)

- Potential of Exp-6 type, fitted to reproduce Hugoniot curves

$$\mathcal{E} - \mathcal{E}_0 - \frac{1}{2}(\mathcal{P} + \mathcal{P}_0)(\mathcal{V}_0 - \mathcal{V}) = 0$$

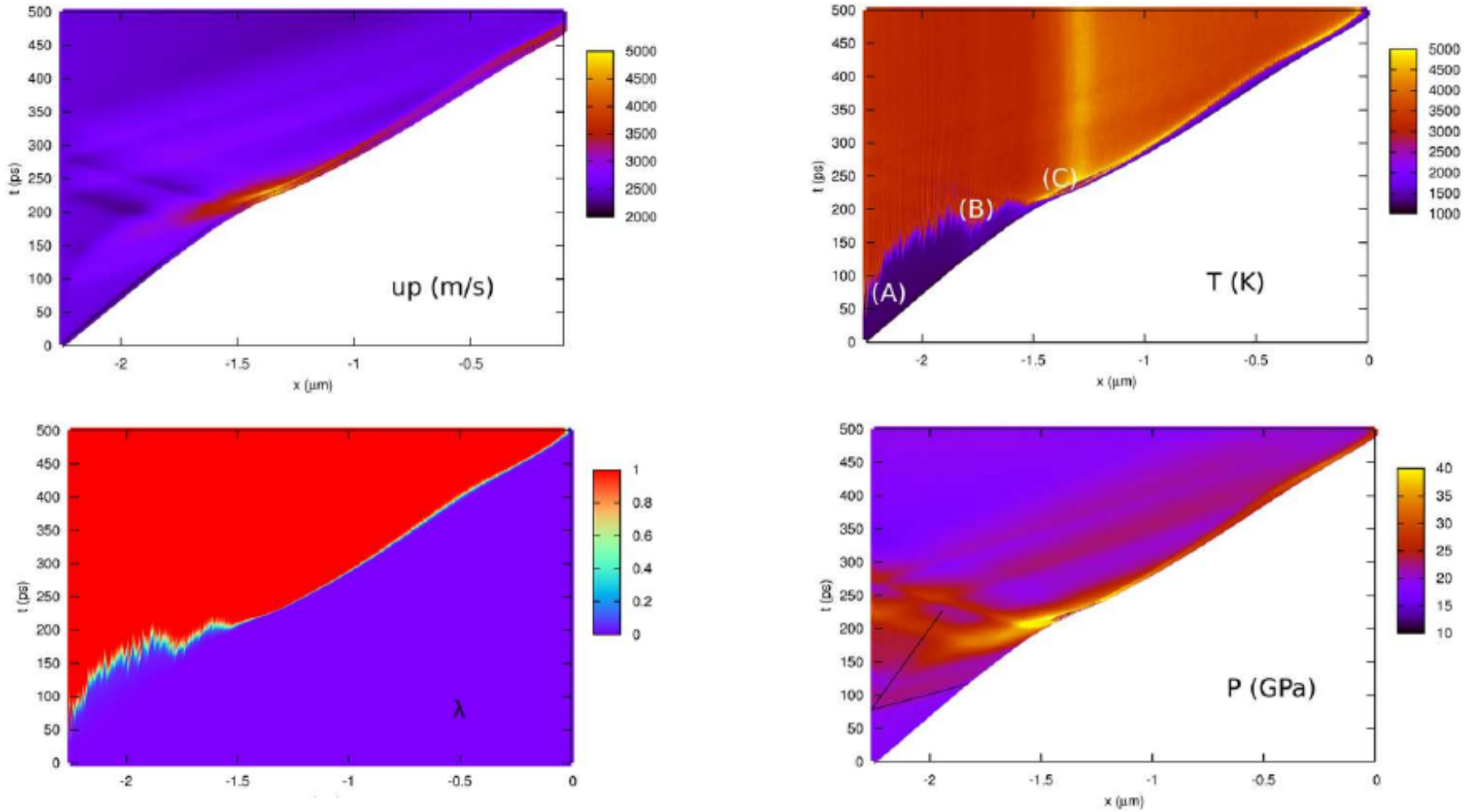
- C_v taken from thermodynamic tables

- σ so that equilibration time between internal and external degrees of freedom is of the order of a few ps

- Modeling of chemical reactions through some progress variables λ_i

- System of length ~ 4.5 μm

Detonation waves in nitromethane (2)



Particle velocity, temperature, progress variable, pressure

J.-B. Maillet, G. Vallverdu, N. Desbiens and G. Stoltz, *Europhys. Lett.* (2011)

Coupling with higher scales

Coarse-graining even further: SDPD (1)

- Adding thermal fluctuations to particle discretization of Navier–Stokes[13]
- Size K of particles (masses Km_*)
- Variables: (q, p) position of discretization nodes, entropy S_i or energy ε_i
- Conservative part of the dynamics: Hamiltonian dynamics with energy

$$\mathcal{E}(q,p,S) = \sum_{i=1}^{N} \varepsilon_i\big(S_i, \rho_i(q)\big) + \frac{p_i^2}{2m}, \qquad \rho_i(q) = \sum_{j=1}^{N} mW(r_{ij})$$

$$\begin{cases} dq = \dfrac{p}{m}\,dt, \\ dp = -\nabla_q \mathcal{E}(q,p,S)\,dt, \\ dS = 0. \end{cases}$$

[13] P. Español and M. Revenga, *Phys. Rev. E* (2003)

Coarse-graining even further: SDPD (2)

- Fluctuation/dissipation: energy formulation[14]

$$\begin{cases} dp_i = -\gamma_{ij}^{\theta} P_{ij}^{\theta} v_{ij}\, dt + \sigma_{ij}^{\theta} P_{ij}^{\theta}\, dB_{ij}, \\ dp_j = -dp_i, \\ d\varepsilon_i = \dfrac{1}{2}\left[\gamma_{ij}^{\theta} v_{ij}^T P_{ij}^{\theta} v_{ij} - \dfrac{(\sigma_{ij}^{\theta})^2}{m}\mathrm{Tr}(P_{ij}^{\theta})\right] dt - \dfrac{1}{2}\sigma_{ij}^{\theta} v_{ij}^T P_{ij}^{\theta}\, dB_{ij}, \\ d\varepsilon_j = d\varepsilon_j, \end{cases}$$

with appropriate choices for $\gamma_{ij}^{\parallel}, \gamma_{ij}^{\perp}, \sigma_{ij}^{\perp}, \sigma_{ij}^{\parallel}$ to ensure the invariance of

$$\mu(dq\, dp\, d\varepsilon) = g\left(E(q,p,\varepsilon), \sum_{i=1}^{N} p_i\right) \prod_{i=1}^{N} \frac{\exp\left(\frac{S_i(\varepsilon_i,q)}{k_{\mathrm{B}}}\right)}{T_i(\varepsilon_i,q)}\, dq\, dp\, d\varepsilon$$

- Reduces to Smoothed Particle Hydrodynamics when $\sigma_{ij} = 0$

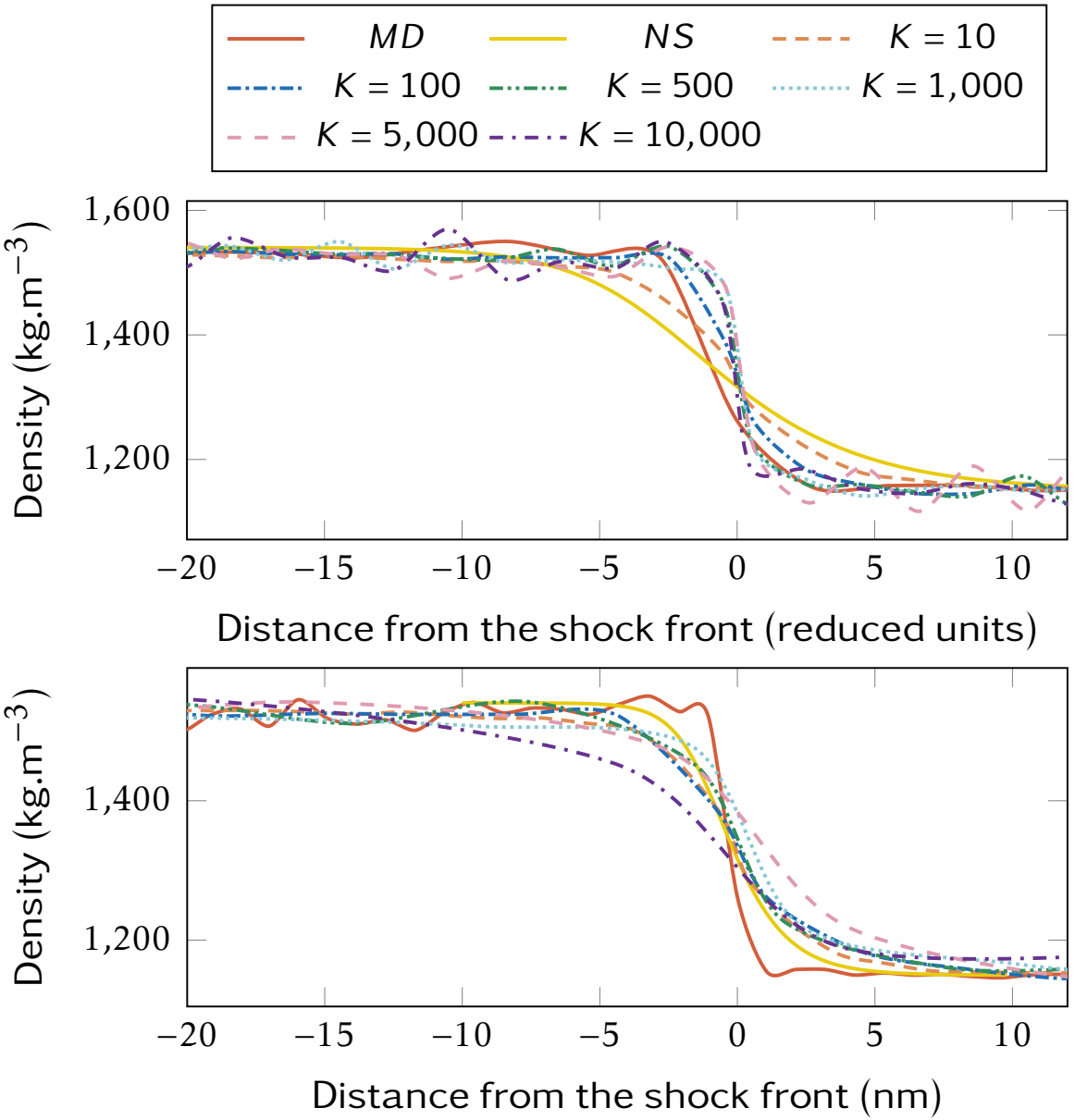
[14] G. Faure, J.-B. Maillet and G. Stoltz, *Phys. Rev. E* (2016)

Parametrization of SDPD

- **Free energy** $\mathscr{F}(\rho, T)$, computed from NVT simulations. Deduce...
  - energy $\mathcal{E}(\rho, T) = -T^2 \partial_T \left(\dfrac{\mathscr{F}(\rho, T)}{T} \right)$
  - entropy $\mathcal{S}(\rho, T) = \dfrac{\mathcal{E}(\rho, T) - \mathscr{F}(\rho, T)}{T}$
  - pressure $\mathcal{P}(\rho, T) = \rho^2 \partial_\rho \mathscr{F}(\rho, T)$
  - heat capacity $\mathcal{C}(\rho, T) = \partial_T \mathcal{E}(\rho, T)$

- **Fluid viscosities**, which appear in γ_{ij}, σ_{ij}

SDPD: some numerical results



Conclusion

Conclusion and perspectives

- Coarse-grained models for atomistic simulations

- **Dissipative Particle Dynamics with conserved energy (DPDE)**
  - can be used in nonequilibrium situations
  - replace a molecule or some group of atoms by a mesoparticle
  - consistent thermodynamics
  - input: static properties (computed ab-initio) and dynamical parameters

- **Smoothed Dissipative Particle Dynamics (SDPD)**
  - hydrodynamics-like (*e.g.* solvent in bulk-like regime)...
  - ... but particle-based: seamless coupling with DPDE can be envisioned![15]

[15] Work in progress with Gérôme Faure, Jean-Bernard Maillet (CEA/DAM) and Pep Español (UNED Madrid).