Sampling constraints in average: The example of Hugoniot curves

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Microscopic description of physical systems

- Positions q (configuration), momenta $p = M\dot{q}$ (M diagonal mass matrix)
- Microstate for N particle system: $(q,p) = (q_1,\dots,q_N,\ p_1,\dots,p_N) \in \mathcal{D}^N \times \mathbb{R}^{dN}$
- Hamiltonian $H(q,p) = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + V(q_1,\dots,q_N)$
- All the physics is contained in V! For instance, pair interactions $V(q_1,\dots,q_N) = \sum_{1\le i<j\le N} v(|q_j - q_i|)$
- Canonical ensemble = probability measure on (q,p) (average energy fixed)

$$\mu_{|\mathcal{D}|,T}(dq\,dp) = Z_{|\mathcal{D}|,T}^{-1}\, \mathrm{e}^{-\beta H(q,p)}\, dq\, dp, \qquad \beta = \frac{1}{k_{\mathrm{B}}T}$$

- Thermodynamic properties: $\langle A\rangle_{|\mathcal{D}|,T} = \int A(q,p)\,\mu_{|\mathcal{D}|,T}(dq\,dp)$

Sampling the canonical measure

- SDE on the configurational part only (momenta trivial to sample)

$$dq_t = -\nabla V(q_t)\,dt + \sigma dW_t, \qquad (1)$$

where $(W_t)_{t\ge 0}$ is a standard Wiener process of dimension dN

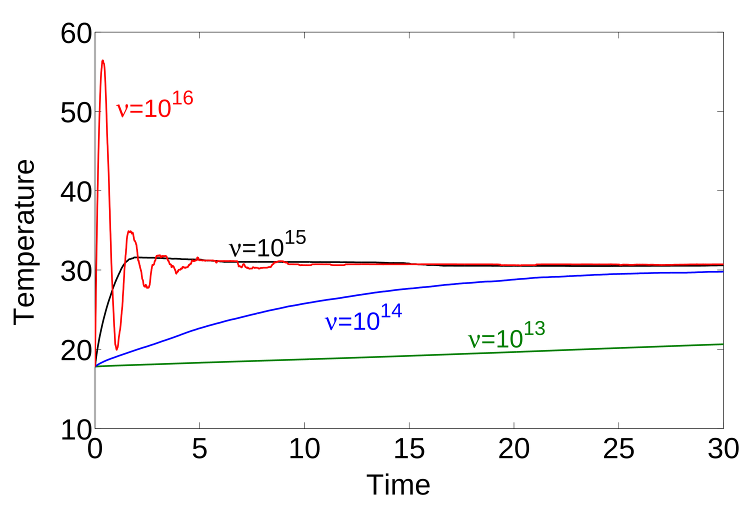
- Associated Fokker-Planck equation $\partial_t\psi = \mathrm{div}\left(\nabla V\psi + \frac{\sigma^2}{2}\nabla\psi\right)$ where $\psi(t,\cdot)$ is the law of q_t
- Invariance of the marginal in positions of the canonical measure $\nu(dq) = Z^{-1}\,\mathrm{e}^{-\beta V(q)}\,dq$, when the fluctuation/dissipation relation $\sigma = \sqrt{\frac{2}{\beta}}$ is satisfied
- Invariance + irreducibility (elliptic process): $\lim_{T\to\infty} \frac{1}{T}\int_0^T A(q_t)\,dt = \int A(q)\,d\nu$ a.s.
- Several notions of convergence: here, longtime convergence in law
- Rewrite the Fokker-Planck equation as $\partial_t\psi = \frac{1}{\beta}\mathrm{div}\left(\psi_\infty \nabla\left(\frac{\psi}{\psi_\infty}\right)\right)$ with the invariant measure $\psi_\infty = Z^{-1}\exp(-\beta V)$
- Define the relative entropy $\mathcal{H}(\psi(t,\cdot)\,|\,\psi_\infty) = \int \ln\left(\frac{\psi(t,\cdot)}{\psi_\infty}\right)\psi_\infty$
- It holds $\|\psi(t,\cdot) - \psi_\infty\|_{TV} \le \sqrt{2\mathcal{H}(\psi(t,\cdot)\,|\,\psi_\infty)}$. The aim is therefore to show that the entropy converges to 0.
- A simple computation shows $\frac{d}{dt}H(\psi(t,\cdot)\,|\,\psi_\infty) = -\beta^{-1} I(\psi(t,\cdot)\,|\,\psi_\infty)$ where the Fisher information is $I(\psi(t,\cdot)\,|\,\psi_\infty) = \int \left|\nabla \ln\left(\frac{\psi(t,\cdot)}{\psi_\infty}\right)\right|^2 \psi_\infty$
- When a Logarithmic Sobolev Inequality holds for ψ_∞, namely $H(\phi|\,\psi_\infty) \le \frac{1}{2R} I(\phi\,|\,\psi_\infty)$, then, by Gronwall's lemma, the relative entropy converges exponentially fast to 0, as well as the total variation distance
- Obtaining LSI: Bakry-Emery criterion (convexity), Gross (tensorization), Holley-Stroock's perturbation result
- Other framework: L^2 estimates and Poincaré inequalities

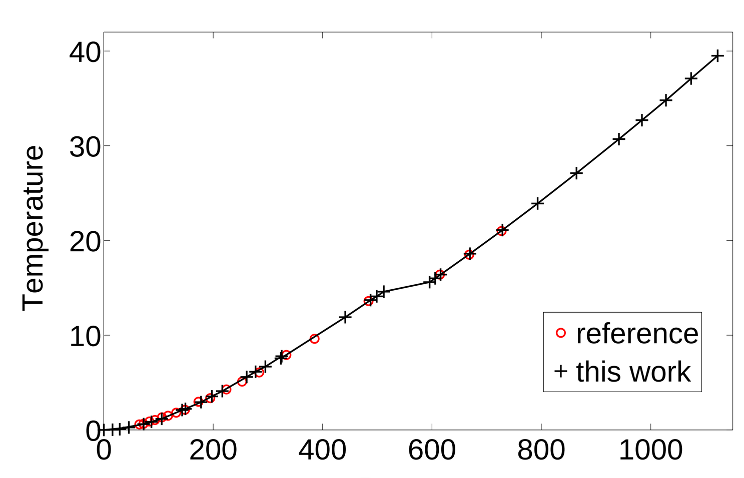
Numerical results

- Multiple replica implementation (interacting only through the update of their common temperature)
- In many codes, ergodic limits for a single replica are easier to implement. The temperature is now random:

$$\begin{cases} dq_t = -\nabla V(q_t)\,dt + \sqrt{2k_{\mathrm{B}}T_t}\,dW_t, \\ dT_t = -\gamma\left(\dfrac{\int_0^t A(q_s)\,\delta_{T_t - T_s}\,ds}{\int_0^t \delta_{T_t - T_s}\,ds}\right)dt, \end{cases}$$

- Obtain orders of magnitude for γ using non-dimensional evolution: $d\left(\frac{T_t}{T_{\mathrm{ref}}}\right) = -\frac{\mathcal{A}_t(T_t)}{Nk_{\mathrm{B}}T_{\mathrm{ref}}}\,\nu\,dt$





Left: Temperature as a function of time (in reduced units) for different values of the frequency ν (in s^{-1}), for a system of size $N = 4{,}000$, and a fixed compression $c = 0.62$. Pole: $T_0 = 10$ K, $\rho_0 = 1.806\times 10^3$ kg/m^3 (so that $P_0 \simeq 0$). Right: Hugoniot curve.

References

[1] T. Lelievre, M. Rousset and G. Stoltz, *Free-Energy Computations: A Mathematical Perspective* (Imperial College Press, 2010)

[2] J. B. Maillet and G. Stoltz, Sampling constraints in average: The example of Hugoniot curves, *Appl. Math. Res. Express* **2008** abn004 (2009)

[3] J. B. Maillet, M. Mareschal, L. Soulard, R. Ravelo, P. S. Lomdahl, T.C . Germann, and B. L. Holian, Uniaxial Hugoniot: A method for atomistic simulations of shocked materials, *Phys. Rev. E*, **63** 016121 (2000).

Physical motivation

- Hugoniot curve = all admissible shocks as given by the third equation of the Rankine-Hugoniot relations for fluids described by the Euler equation ($\mathcal{E}$ internal energy, $\mathcal{P}$ pressure, $\mathcal{V}$ volume): $\mathcal{E} - \mathcal{E}_0 - \frac{1}{2}(\mathcal{P}+\mathcal{P}_0)(\mathcal{V}_0 - \mathcal{V}) = 0$
- Statistical physics reformulation: reference temperature T_0, simulation cell $\mathcal{D}_c = cL\mathbb{T}\times(L\mathbb{T})^2$ with $c = 1$ at the pole → vary the compression rate in the x direction $c = |\mathcal{D}|/|\mathcal{D}_0|$
- Consider the observable $A_c(q,p) = H(q,p) - \langle H\rangle_{|\mathcal{D}_0|,T_0} + \frac{1}{2}(P_{xx}(q,p) + \langle P\rangle_{|\mathcal{D}_0|,T_0})(1-c)|\mathcal{D}_0|$ where the xx component of the pressure tensor is $P_{xx}(q,p) = \frac{1}{|\mathcal{D}|}\sum_{i=1}^{N} \frac{p_{i,x}^2}{m_i} - q_{i,x}\partial_{q_{i,x}} V(q)$
- For a given compression with $c_{\max} \le c \le 1$, find $T \equiv T(c)$ such that

$$\langle A_c\rangle_{|\mathcal{D}_c|,T} = 0$$

Sampling constraints in average

- Set some external parameter (temperature, pressure/volume) to obtain the right value of a given thermodynamic property. For instance, vary the temperature in the canonical ensemble
- Given some observable A, the problem then reads

$$\boxed{\text{Find } T \text{ such that } \langle A\rangle_T = 0}$$

- Since the momenta are straightforward to sample, there is no restriction in considering $A \equiv A(q)$

$$f(T) = \langle A\rangle_T = \int A(q)\,\mu_T(dq), \qquad \mu_T(q) = \frac{1}{Z_T}\exp\left(-\frac{V(q)}{k_{\mathrm{B}}T}\right), \qquad Z_T = \int \exp\left(-\frac{V(q)}{k_{\mathrm{B}}T}\right) dq,$$

- Several methods to find the zero of the function $f(T) = \langle A\rangle_T$ (Newton strategy, but requires the computation of the derivative, difficult to converge because of statistical error; New thermodynamic ensemble = (unknown) ergodic limit of dedicated dynamics such as [3])
- Another idea: Assume that there exists an interval $I_T = [T_{\min}, T_{\max}]$, a temperature $T^* \in (T_{\min}, T_{\max})$, and constants $a, \alpha > 0$ such that

$$\langle A\rangle_T = 0 \Leftrightarrow T = T^* \quad \text{and} \quad \alpha \le \frac{\langle A\rangle_T - \langle A\rangle_{T^*}}{T - T^*} \le a$$

- Note that the (deterministic) dynamics $T'(t) = -\gamma\,\langle A\rangle_{T(t)}$ is such that $T(t) \to T^*$, and that the dynamics (1) is ergodic for the canonical measure at temperature T
- Approximate the equilibrium canonical expectation by the current one:

$$\boxed{\begin{aligned} dq_t &= -\nabla V(q_t)\,dt + \sqrt{2k_{\mathrm{B}}T(t)}\,dW_t, \\ T'(t) &= -\gamma\,\mathbb{E}(A(q_t)), \end{aligned}} \qquad (2)$$

- Note that (T^*, μ_{T^*}) is invariant

Convergence of the nonlinear dynamics (2)

- Nonlinear PDE on the law ψ of the process q_t

$$\begin{cases} \partial_t\psi = k_{\mathrm{B}}T(t)\,\nabla\cdot\left[\mu_{T(t)}\nabla\left(\dfrac{\psi}{\mu_{T(t)}}\right)\right] = k_{\mathrm{B}}T(t)\,\Delta\psi + \nabla\cdot(\psi\nabla V), \\ T'(t) = -\gamma\displaystyle\int A(q)\,\psi(t,q)\,dq \end{cases} \qquad (3)$$

- Assule that the family of measures $\{\mu_T\}_{T\in I_T}$ satisfies a logarithmic Sobolev inequality (LSI) with a uniform constant $1/\rho$, namely

$$\int \Big(f\ln f - f + 1\Big)\mu_T \le \frac{1}{\rho}\int \frac{|\nabla f|^2}{f}\,\mu_T.$$

Theorem 1 (Short-time existence/uniqueness) *Assume that the observable $A \in \mathrm{C}^3$ and $V \in \mathrm{C}^2$. For a given initial condition (T^0, ψ^0), with $T^0 > 0$ and $\psi^0 \in \mathrm{H}^2$, $\psi^0 \ge 0$, $\int \psi^0 = 1$, there exists a time $\tau \ge \frac{T^0}{2\gamma\|A\|_\infty} > 0$ such that (3) has a unique solution $(T,\psi) \in \mathrm{C}^1([0,\tau],\mathbb{R}) \times \mathrm{C}^0([0,\tau],\mathrm{H}^2)$. In particular, the temperature remains positive.*

Theorem 2 *Consider an initial data (T^0, ψ^0) with $\psi^0 \in \mathrm{H}^2$, $\psi^0 \ge 0$, $\int \psi^0 = 1$, and associated entropy $\mathcal{E}(0) \le \mathcal{E}^*$, where*

$$\mathcal{E}^* = \inf\left\{\frac{1}{2}(T_{\min} - T^*)^2, \frac{1}{2}(T_{\max} - T^*)^2\right\}.$$

Then, there exists $\gamma_0 > 0$ such that, for all $0 < \gamma \le \gamma_0$, (3) has a unique solution $(T,\psi) \in \mathrm{C}^1([0,\tau],\mathbb{R}) \times \mathrm{C}^0([0,\tau],\mathrm{H}^2)$ for all $\tau \ge 0$, and the entropy converges exponentially fast to zero: There exists $\kappa > 0$ (depending on γ) such that

$$\mathcal{E}(t) \le \mathcal{E}(0)\exp(-\kappa t).$$

In particular, the temperature remains positive at all times: $T(t) \ge T_{\min} > 0$, and it converges exponentially fast to T^*.

- Proof of Theorem 1: Schauder fixed-point theorem using a mapping $T \mapsto \psi_T \mapsto g(T)$
- Proof of Theorem 2: entropy estimates using the total entropy $\mathcal{E}(t) = E(t) + \frac{1}{2}(T(t) - T^*)^2$, where the reference measure in the spatial entropy is time-dependent: $E(t) = \int (f\ln f - f + 1)\mu_{T(t)}$ with $f = \frac{\psi}{\mu_{T(t)}}$
- The proof relies on the estimates $|T'(t)| \le \gamma\left(a\,|T(t) - T^*| + \|A\|_\infty\sqrt{2E(t)}\right)$ and

$$E'(t) \le -\left(\rho k_{\mathrm{B}}T(t) - \frac{2|T'(t)|\,\|V\|_\infty}{k_{\mathrm{B}}T(t)^2}\right)E(t) + \frac{2\sqrt{2}|T'(t)|\|V\|_\infty}{k_{\mathrm{B}}T(t)^2}\sqrt{E(t)}$$

so that a Gronwall inequality can be shown to hold for $\mathcal{E}$ upon choosing γ small enough (since $T' \propto \gamma$)