SI: Programming entropy production hotspots via interaction patterning

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1. Fluid driven through a nanopore

1.1. Equations of motion for the system

The equations of motion for the wall and fluid particles are given by

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + c_i F_e \mathbf{e}_x - S_i \left[\alpha \mathbf{p}_i + k \left(\mathbf{q}_i - \mathbf{q}_{0,i}\right)\right] \end{aligned} \tag{1}$$

in which $\mathbf{q}_i$, $\mathbf{p}_i$, m_i, and $c_i = (-1)^i$ denote the position, momentum, mass ($m_i = 1$ for all particles) and color charge of particle i ($c_i = 0$ for a wall particle), S_i a parameter equal to 1 for a wall particle and 0 otherwise, $\mathbf{F}_i$ the force exerted on particle i by the other particles, F_e the strength of the color field exerted along the x axis of unit vector $\mathbf{e}_x$, k the spring constant that tethers the wall atom to its lattice position $\mathbf{q}_{0,i}$. The $-(S_i \alpha \mathbf{p}_i)$ term ensures

that the internal energy of the system is kept constant and is obtained by applying Gauss' principle of least constraint.[1] The equation defining the ergostat multiplier α can be obtained by writing the condition for which the internal energy is conserved or, in other words, when the rate of change of the internal energy is zero.

The internal energy of the system is obtained from the Hamiltonian as[1]

$$\mathcal{H} = \sum_i \frac{\mathbf{p}_i^2}{2m_i} + \frac{1}{2}\sum_i \sum_{j\neq i} \phi(q_{ij}) + \sum_i \frac{k}{2} S_i \left(\mathbf{q}_i - \mathbf{q}_{0,i}\right)^2 \tag{2}$$

and the rate of change in internal energy is thus given by

$$\dot{\mathcal{H}} = \sum_i \frac{\dot{\mathbf{p}}_i \cdot \mathbf{p}_i}{m_i} + \sum_i \dot{\mathbf{q}}_i \left[\nabla_i \sum_{j\neq i} \phi(q_{ij})\right] + \sum_i k S_i \dot{\mathbf{q}}_i \cdot \left(\mathbf{q}_i - \mathbf{q}_{0,i}\right) \tag{3}$$

Denoting by $\mathbf{F}_i = -\nabla_i \sum_{j\neq i} \phi(q_{ij})$ the force exerted on particle i by the other particles ($j \neq i$), we obtain

$$\dot{\mathcal{H}} = \sum_i \frac{\dot{\mathbf{p}}_i \cdot \mathbf{p}_i}{m_i} - \sum_i \mathbf{F}_i \cdot \frac{\mathbf{p}_i}{m_i} + \sum_i k S_i \frac{\mathbf{p}_i}{m_i} \cdot \left(\mathbf{q}_i - \mathbf{q}_{0,i}\right) \tag{4}$$

Replacing $\dot{\mathbf{p}}_i$ by the second line of Eq. 16, we obtain

$$\begin{aligned} \dot{\mathcal{H}} &= \sum_i \frac{c_i F_e p_{x,i}}{m_i} - \sum_i S_i \frac{\alpha \mathbf{p}_i^2}{m_i} \\ &= F_e J_x - 2\alpha K_w \end{aligned} \tag{5}$$

in which $J_x = \sum_i c_i p_{x,i}/m_i$ denotes the instantaneous current along the $\mathbf{x}$ axis, and $K_w = \sum_i S_i \frac{\mathbf{p}_i^2}{m_i}$ denotes the kinetic energy for the wall. If we denote N_w as the number of atoms in the wall, the application of the equipartition principle then leads to $K_w = N_w/\beta$, in which $\beta = (k_B T)^{-1}$ is the reciprocal temperature. Since we use an ergostat, $\dot{\mathcal{H}} = 0$, leading to the

following mathematical expression for α as

$$\alpha = \frac{F_e J_x}{\sum_i S_i \frac{\mathbf{p}_i^2}{m_i}} \tag{6}$$

1.2. Mathematical expression for entropy production

As discussed by Searles *et al.*,[2] the dissipation Ω and rate of entropy production $\dot{\Sigma}$ are equivalent for a system with $\dot{\mathcal{H}} = 0$. The dissipation function[3] can be obtained from the equations of motion according to

$$\begin{aligned} \Omega(\mathbf{\Gamma}(t)) &= \beta \frac{d\mathcal{H}(\mathbf{\Gamma}(t))}{dt} - \Lambda(\mathbf{\Gamma}(t)) \\ &= -\Lambda(\mathbf{\Gamma}(t)) \\ &= \dot{\Sigma}(\mathbf{\Gamma}(t)) \end{aligned} \tag{7}$$

in which $\mathbf{\Gamma} = (\mathbf{q}, \mathbf{p})$ denotes a phase space point and $\Lambda = \left(\frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} \right)$ the phase space compression factor. The phase space compression factor $\Lambda(\mathbf{\Gamma})$ given by

$$\begin{aligned} \Lambda(\mathbf{\Gamma}) &= \frac{\partial}{\partial \mathbf{\Gamma}} \cdot \dot{\mathbf{\Gamma}} \\ &= \sum_i \frac{\partial \dot{\mathbf{q}}_i}{\partial \mathbf{q}_i} + \sum_i \frac{\partial \dot{\mathbf{p}}_i}{\partial \mathbf{p}_i} \\ &= -2 \sum_i \alpha S_i \\ &= -2 N_w \alpha \\ &= -\beta(\mathbf{\Gamma}) F_e J_x \end{aligned} \tag{8}$$

in which we have used the last line of Eq. 5 and $\beta K_w = N_w$. This block of equations shows that the phase space compression factor can be written as a function of the number of wall atoms and the ergostat multiplier ($-2N_w\alpha$) in the second and third line of Eq. (8) or as a function of the current ($-\beta(\mathbf{\Gamma})F_e J_x$) in the fourth line of Eq. (8). Since we are focusing on

the dissipation and entropy production that take place in the flowing fluid, we use the latter in the rest of this work. The dissipation and rate of entropy production are then given by

$$\Omega(\mathbf{\Gamma}(t)) = \beta(\mathbf{\Gamma}(t)) J_x F_e = \dot{\Sigma}(\mathbf{\Gamma}(t)) \tag{9}$$

1.3. Equation for local entropy production

The rate of entropy production $\dot{\Sigma}_L$ in a region $\mathcal{L}$ with a characteristic length L is given by

$$\dot{\Sigma}_L = \beta J_{x,L} F_e \tag{10}$$

in which $J_{x,L} = \sum_{i \in \mathcal{L}} c_i p_{x,i}/m_i$

The local entropy production $\Sigma_{L,t}$ measured over a trajectory of duration t is obtained by integrating Eq. 10 with respect to time as follows

$$\Sigma_{L,t} = \int_0^t \dot{\Sigma}_L(\mathbf{\Gamma}(t)) dt \tag{11}$$

and is then averaged over a large set of trajectories, typically 2×10^5 trajectories in this work.

Since there exists many possible ways of partitioning entropy production into local regions, it is important to verify that the results obtained for the local entropy production satisfy a local version of the fluctuation theorem. The local fluctuation theorem [4–6] measures the ratio of the probability of observing a trajectory associated with a positive entropy production equal to A to the probability of observing a trajectory leading to a negative entropy production equal to $(-A)$ and is given by

$$\ln \left[\frac{p\left(\Sigma_{L,t} = A\right)}{p\left(\Sigma_{L,t} = -A\right)} \right] = \left[1 + \kappa_{L,t}\right] A \tag{12}$$

where $\kappa_{L,t}$ captures the correlation between the entropy production in the local region, $\Sigma_{L,t}$,

and in the rest of the system, $\Sigma^*_{L,t}$, as follows.

$$\kappa_{L,t} = \frac{\left\langle \Sigma^*_{L,t}\Sigma_{L,t}\right\rangle - \left\langle \Sigma^*_{L,t}\right\rangle \left\langle \Sigma_{L,t}\right\rangle}{\left\langle \Sigma^2_{L,t}\right\rangle - \left\langle \Sigma_{L,t}\right\rangle^2} \tag{13}$$

1.4. Interaction potentials

The interactions between particles are based on the Weeks-Chandler-Andersen (WCA)[7] modification of the Lennard-Jones potential. The interaction between two particles labeled by i and j is given by

$$\phi(r_{ij}) = 4\epsilon\left[\left(\frac{\sigma}{r_{ij}}\right)^{12} - \left(\frac{\sigma}{r_{ij}}\right)^{6}\right] + \epsilon \tag{14}$$

in which r_{ij} is the distance between two particles i and j, and σ and ϵ denote the exclusion diameter and the interaction strength, respectively, for the WCA potential. Throughout the manuscript, the simulation parameters and results are given in the conventional system of reduced units[8] with σ as the unit of length, ϵ as the unit of energy, and m as the unit of mass. The WCA spherical cutoff radius r_c for the calculation of the interactions is set to $r_c = 2^{1/6}\sigma$. The WCA potential is a short-range repulsive potential. Interactions between two wall particles, two fluid particles, or between a repulsive wall particle and a fluid particle are all modeled with a WCA potential. As a first interaction pattern, we define an attractive patch of width w located in the center of the system. Interactions between an attractive wall particle (a wall atom such that $|x| < w/2$) and a fluid particle are modeled with a Lennard-Jones potential

$$\phi(r_{ij}) = 4\epsilon_{wf}\left[\left(\frac{\sigma_{wf}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{wf}}{r_{ij}}\right)^{6}\right] + \phi(r_{c,wf}) \tag{15}$$

To study the impact of the interaction strength, we vary ϵ_{wf} and $r_{c,wf} = 2.5\sigma$, while keeping $\sigma_{wf} = \sigma$. We then revert the interaction pattern by introducing a repulsive patch within an attractive wall.

2. Fluid driven past an interaction patterned-object

2.1. Equations of motion

The equations of motion are the same as in the first case, with the exception that the particles composing the object play the same role as the wall particles. We therefore have the same set of equations of motion as previously and given by

$$\begin{aligned} \dot{\mathbf{q}}_i &= \frac{\mathbf{p}_i}{m_i} \\ \dot{\mathbf{p}}_i &= \mathbf{F}_i + c_i F_e \mathbf{e}_x - S_i \left[\alpha \mathbf{p}_i + k \left(\mathbf{q}_i - \mathbf{q}_{0,i}\right)\right] \end{aligned} \tag{16}$$

in which S_i denotes a parameter equal to 1 for a motif particle and 0 otherwise. As a result, the equations for the entropy production are the same as for the previous system.

The interaction patterned-object consists of the letters U, M, and L, placed at the center of the system. To program an entropy production cold spot in the central band of the system, we set the particles composing the letter M to be (Lennard-Jones) attractive particles and the particles from the letters U and L to be (WCA) repulsive. To program an entropy production hotspot, we revert the interaction pattern with a letter M composed of (WCA) repulsive particles and the letters U and L composed of attractive (Lennard-Jones) particles.

3. Simulation parameters

We use the same simulation method as in previous work.[6] The dissipation function and entropy production are integrated over 2×10^5 nonequilibrium molecular dynamics trajectories, each starting from a different initial equilibrium configuration. As in previous work,[1,6,9] the equations of motion are propagated with a fourth-order Runge-Kutta integrator and a timestep of 5×10^{-4} time units.For the confined fluid driven out-of-equilibrium, we consider a rectangular simulation cell with $L_x = 50.6$ and $L_y = 12.86$, $N_{wall} = 128$, placed on a 2D face-centered cubic lattice, $N_{fluid} = 192$, a spring constant for the wall potential $k = 250$,

an external field set to $F_e = 0.2$, a total energy for the system of 400, and a total of 2×10^5 trajectories of duration $t = 5$ time units. We vary the width of the attractive region (w) and the interaction strength parameter (ϵ) for the wall particles belonging to the attractive patch as specified in the manuscript. For the second system, we also have a rectangular simulation cell $L_x = 90$ and $L_y = 14$, a number of particles in the letters U, M, and L of $N_{letters} = 61$, a number of fluid particles set to $N_{fluid} = 440$, an external field set to $F_e = 0.2$, a total energy of 200, and 2×10^5 trajectories of duration $t = 5$ time units. We use the conventional periodic boundary conditions are also applied to all systems.[8]

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4. Supporting tables for the data reported in the manuscript

Table 1: Properties in the 5 local regions for a fluid driven through a repulsive nanochannel with an attractive patch with $\epsilon = 2$ and $w = 10$ (Fig. 2). x denotes the x-coordinate for the center of the local region, Ω the local dissipation, J_x the local current, and n the local number density. Statistical uncertainties are of the order of $1 \times 1-^{-3}$ for Ω, 7×10^{-4} for J_x, and 5×10^{-5} for n.

x	Ω	J_x	n
-20.24	3.05	6.53×10^{-2}	0.38
-10.12	2.99	6.41×10^{-2}	0.39
0.00	2.62	5.62×10^{-2}	0.46
10.12	2.99	6.41×10^{-2}	0.39
20.24	3.05	6.53×10^{-2}	0.38

Table 2: Properties in the 5 local regions for a fluid driven through a repulsive nanochannel without an attractive patch (w/o patch) and for $\epsilon = 1, 3, 4, 5$ and $w = 10$ (Fig. 3).

Strength	x	Ω	J_x	n
w/o patch	-20.24	3.50	6.73×10^{-2}	0.40
	-10.12	3.53	6.77×10^{-2}	0.40
	0.00	3.52	6.76×10^{-2}	0.40
	10.12	3.53	6.77×10^{-2}	0.40
	20.24	3.50	6.73×10^{-2}	0.40
$\epsilon = 1$	-20.24	3.32	6.66×10^{-2}	0.39
	-10.12	3.32	6.66×10^{-2}	0.39
	0.00	3.06	6.13×10^{-2}	0.43
	10.12	3.32	6.66×10^{-2}	0.39
	20.24	3.32	6.66×10^{-2}	0.39
$\epsilon = 3$	-20.24	2.81	6.46×10^{-2}	0.38
	-10.12	2.76	6.36×10^{-2}	0.39
	0.00	2.35	5.42×10^{-2}	0.47
	10.12	2.76	6.36×10^{-2}	0.39
	20.24	2.81	6.46×10^{-2}	0.38
$\epsilon = 4$	-20.24	2.55	6.27×10^{-2}	0.38
	-10.12	2.52	6.20×10^{-2}	0.39
	0.00	2.11	5.19×10^{-2}	0.47
	10.12	2.52	6.20×10^{-2}	0.39
	20.24	2.55	6.27×10^{-2}	0.38
$\epsilon = 5$	-20.24	2.36	6.17×10^{-2}	0.37
	-10.12	2.33	6.08×10^{-2}	0.39
	0.00	1.94	5.08×10^{-2}	0.48
	10.12	2.33	6.08×10^{-2}	0.39
	20.24	2.36	6.17×10^{-2}	0.37

Table 3: Properties in the 5 local regions for a fluid driven through an attractive nanochannel with a repulsive patch for $\epsilon = 1, 2, 3, 4, 5$ and $w = 10$ (Fig. 4).

Strength	x	Ω	J_x	n
	-20.24	2.69	5.97×10^{-2}	0.41
	-10.12	2.71	6.02×10^{-2}	0.41
$\epsilon = 1$	0.00	2.92	6.48×10^{-2}	0.37
	10.12	2.71	6.02×10^{-2}	0.41
	20.24	2.69	5.97×10^{-2}	0.41
	-20.24	2.02	5.38×10^{-2}	0.41
	-10.12	2.04	5.49×10^{-2}	0.41
$\epsilon = 2$	0.00	2.30	6.14×10^{-2}	0.36
	10.12	2.04	5.49×10^{-2}	0.41
	20.24	2.02	5.38×10^{-2}	0.41
	-20.24	1.59	5.04×10^{-2}	0.42
	-10.12	1.61	5.09×10^{-2}	0.41
$\epsilon = 3$	0.00	1.82	5.76×10^{-2}	0.35
	10.12	1.61	5.09×10^{-2}	0.41
	20.24	1.59	5.04×10^{-2}	0.42
	-20.24	1.29	4.75×10^{-2}	0.42
	-10.12	1.30	4.78×10^{-2}	0.41
$\epsilon = 4$	0.00	1.49	5.48×10^{-2}	0.34
	10.12	1.30	4.78×10^{-2}	0.41
	20.24	1.29	4.79×10^{-2}	0.41
	-20.24	1.07	4.49×10^{-2}	0.42
	-10.12	1.08	4.54×10^{-2}	0.42
$\epsilon = 5$	0.00	1.25	5.24×10^{-2}	0.34
	10.12	1.08	4.54×10^{-2}	0.42
	20.24	1.07	4.49×10^{-2}	0.42

Table 4: Results obtained with an attractive patch of width $w = 2.7$ ($\epsilon = 2$).

x	Ω	J_x	n
-23.968	0.90	5.87×10^{-2}	0.40
-21.305	0.90	5.88×10^{-2}	0.40
-18.642	0.89	5.86×10^{-2}	0.40
-15.979	0.89	5.86×10^{-2}	0.40
-13.316	0.89	5.85×10^{-2}	0.40
-10.653	0.89	5.84×10^{-2}	0.40
-7.989	0.89	5.87×10^{-2}	0.40
-5.326	0.89	5.85×10^{-2}	0.40
-2.663	0.85	5.57×10^{-2}	0.41
0.000	0.80	5.25×10^{-2}	0.45
2.663	0.85	5.57×10^{-2}	0.41
5.326	0.89	5.85×10^{-2}	0.40
7.989	0.89	5.87×10^{-2}	0.40
10.653	0.89	5.84×10^{-2}	0.40
13.316	0.89	5.85×10^{-2}	0.40
15.979	0.89	5.86×10^{-2}	0.40
18.642	0.89	5.86×10^{-2}	0.40
21.305	0.90	5.88×10^{-2}	0.40
23.968	0.90	5.87×10^{-2}	0.40

Table 5: Results obtained with an attractive patch of width $w = 4.6$ ($\epsilon = 2$).

x	Ω	J_x	n
-23.000	1.51	6.05×10^{-2}	0.39
-18.400	1.51	6.04×10^{-2}	0.39
-13.800	1.51	6.07×10^{-2}	0.39
-9.200	1.51	6.05×10^{-2}	0.40
-4.600	1.46	5.87×10^{-2}	0.40
0.000	1.31	5.26×10^{-2}	0.45
4.600	1.46	5.87×10^{-2}	0.40
9.200	1.51	6.05×10^{-2}	0.40
13.800	1.51	6.07×10^{-2}	0.39
18.400	1.51	6.04×10^{-2}	0.39
23.000	1.51	6.05×10^{-2}	0.39

Table 6: Results obtained with an attractive patch of width $w = 7.2$ ($\epsilon = 2$).

x	Ω	J_x	n
-21.686	2.29	6.34×10^{-2}	0.39
-14.457	2.28	6.32×10^{-2}	0.39
-7.229	2.25	6.23×10^{-2}	0.40
0.000	1.98	5.49×10^{-2}	0.45
7.229	2.25	6.23×10^{-2}	0.40
14.457	2.28	6.32×10^{-2}	0.39
21.686	2.29	6.34×10^{-2}	0.39

Table 7: Results obtained with an attractive patch of width $w = 10.1$ ($\epsilon = 2$).

x	Ω	J_x	n
-20.240	3.05	6.53×10^{-2}	0.38
-10.120	2.99	6.45×10^{-2}	0.39
0.000	2.62	5.62×10^{-2}	0.46
10.120	2.99	6.45×10^{-2}	0.39
20.240	3.05	6.53×10^{-2}	0.38

Table 8: Local entropy production obtained with interaction patterning ($\epsilon = 5$) that includes an attractive letter M and repulsive letters U and L (Ω_A) and with the reverse interaction pattern (Ω_R).

x	Ω_A	Ω_R
-40.00	3.77	2.63
-30.00	4.01	2.72
-20.00	3.50	2.34
-10.00	2.26	2.30
0.00	3.79	3.21
10.00	2.30	2.29
20.00	3.51	2.34
30.00	4.02	2.72
40.00	3.78	2.63