Experimental Results: Cases of Spontaneous Order and Separation

Phenomena, References, and Interpretation via Constraint-Reshaped $P_\infty(S;\lambda)$

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This document lists representative cases that satisfy spontaneous order or separation, with brief descriptions of the *experimentally* observed phenomena, standard references, and an interpretation in the theoretical framework of the companion paper *Entropy Has No Direction* (entropy.tex): entropy has no intrinsic direction and is described by a probability distribution $P(S)$; constraints and boundary conditions reshape the long-time entropy distribution $P_\infty(S;\lambda)$; spontaneous low-entropy transitions are possible when the accessible phase space $\mathcal{A}(\lambda)$ and the macrostate volumes $W_m^{(E)}(\lambda)$ are altered by λ. Only actual experiments (or well-known macroscopic phenomena) are cited; simulation work is excluded except for one numerical study (case 17) that illustrates the same constraint-reshaping mechanism in active matter. Experiments from multiple institutions are included (e.g. Qiao–Wang; Siwy and coworkers; Ramirez, Mafe et al.; Experton, Wu, Martin; Powell, Vlassiouk, Siwy; Tsutsui et al.).

1 Cases

1.1 Quasi-one-dimensional ion lineups in nanopores

Constraint. Geometry: effective pore size d_e close to effective ion size d_i ($d_i < d_e < 2d_i$).

Phenomenon. Ions inside the pores form quasi-one-dimensional lineups; collisions are suppressed and the system cannot fully relax to thermodynamic equilibrium.

Reference. Qiao and Wang [3]: nanoporous carbon electrodes in dilute aqueous cesium pivalate (CsPiv); when $d_e \approx 1\,\mathrm{nm}$ and $d_i \approx 0.7\,\mathrm{nm}$, confined ions exhibit quasi-1D ordering.

Interpretation. The geometric constraint λ (nanopore size and shape) restricts the accessible phase space $\mathcal{A}(\lambda)$ and changes the accessible macrostate volumes $W_m^{(E)}(\lambda)$. The long-time distribution $P_\infty^{(E)}(S;\lambda)$ is structurally different from the unconstrained case (sharp criterion in entropy.tex); the system spends substantial probability in lower-entropy (more ordered) configurations.

1.2 Voltage exceeding the second-law limit (asymmetric nanopores)

Constraint. Charged small nanopores with asymmetric geometry.

Phenomenon. The measured potential difference $|\delta V|$ is nearly one order of magnitude larger than the heat-engine upper bound predicted by the traditional second law.

Reference. Qiao and Wang [3]: steady-state potential in charged small nanopores under isothermal conditions far exceeds the conventional thermodynamic limit.

Interpretation. Asymmetric constraint reshapes $P_\infty(S;\lambda)$ so that the steady state is intrinsically out of equilibrium. The observable (voltage) reflects a long-time distribution concentrated in lower-entropy regimes, without requiring a universal "entropy does not decrease" law.

1.3 Spontaneous non-equilibrium domain (SND)

Constraint. Local asymmetric energy barriers produced by the nanopore walls.

Phenomenon. The system spontaneously enters a "spontaneous non-equilibrium domain" (SND), where entropy S remains below the global maximum S_{eq}; the system attains a local maximum entropy $S_{\text{ne}} < S_{\text{eq}}$ under the constraint.

Reference. Qiao and Wang [3]: locally nonchaotic energy barriers prevent relaxation to global equilibrium; the steady state is a non-equilibrium steady state (NESS).

Interpretation. The constraint defines an effective invariant measure on a restricted set of states; $P_\infty(S;\lambda)$ has significant weight at $S < S_{\text{eq}}$. There is no need for "compensating entropy increase" elsewhere; the distribution is reshaped by λ.

1.4 Non-Boltzmann surface ion enrichment

Constraint. Geometry reshapes the accessible phase space $\mathcal{A}(\lambda)$.

Phenomenon. Surface ion density $\sigma^\pm$ does not follow the Boltzmann factor $e^{\mp\beta z e_0 V/2}$; charge accumulates spontaneously in an anomalous way.

Reference. Qiao and Wang [3]: steady-state ion distribution in charged small nanopores deviates from Boltzmann; confinement and asymmetry yield intrinsic nonequilibrium distribution.

Interpretation. Under the constraint λ, the invariant measure (and hence $P_\infty(S;\lambda)$) is not that of the unconstrained Boltzmann equilibrium. The observed enrichment is a consequence of the reshaped distribution, not a violation of the underlying dynamics.

1.5 Useful work from a single heat reservoir in an isothermal cycle

Constraint. Asymmetric constraint that reshapes the entropy distribution.

Phenomenon. The system performs useful work in an isothermal cycle by absorbing heat from a single thermal reservoir, with no other net effect.

Reference. Qiao and Wang [3]: supercapacitive cells with potential differences exceeding the traditional second-law bound allow extraction of work from a single reservoir in a cycle.

Interpretation. In the corrected view, "no work from a single reservoir" is not a universal law but a statement that depends on the long-time entropy distribution. When λ reshapes $P_\infty(S;\lambda)$ so that low-entropy states are more accessible, spontaneous transitions can be harnessed to do work; the Qiao–Wang experiment is a direct experimental validation.

1.6 Geometric rectification in nanofluidic structures

Constraint. Asymmetric geometry in nanopores or nanofluidic channels.

Phenomenon. Ion current rectification (diode-like behaviour): ionic current is larger for one voltage polarity than for the opposite, so ions migrate preferentially in one direction under an applied field; in some setups, spontaneous directional transport or EMF arises from asymmetry without external bias.

References. Experimental observation: Siwy [4] (ion-current rectification in nanopores and nanotubes with broken symmetry; asymmetric I–V curves in conical and pyramidal pores). EOF rectification and AC-driven pump: Experton, Wu, and Martin [5] (ion current and electroosmotic flow rectification in asymmetric nanopore membranes; AC-driven electroosmotic pump). Review of mechanisms and experiments: Zhou et al. [10] (ionic current rectification in asymmetric nanofluidic devices).

Interpretation. Asymmetric λ changes the invariant measure and the induced entropy distribution $P_\infty(S;\lambda)$. Rectification is a kinetic consequence of the same constraint-induced reshaping; the dynamics under λ favour one direction, consistent with a distribution that weights certain (lower-entropy) configurations more than in the unconstrained case.

1.7 Electroosmotic flow rectification and AC-driven pump

Constraint. Asymmetric pore shape (conical or pyramidal) and permselectivity in nanopore membranes.

Phenomenon. Not only ion current but also electroosmotic flow (EOF) is rectified: flow rate depends on the direction of the applied field. An AC voltage with zero time-average can drive a net (time-averaged) fluid flow, enabling an AC-driven electroosmotic pump.

Reference. Experton, Wu, and Martin [5]: asymmetric nanopore membranes (conical pores in polymer, pyramidal in mica); concentration polarization and inverse relation between field and salt concentration in the pore yield EOF rectification; application to AC-driven pumps.

Interpretation. The same asymmetric constraint λ that reshapes $P_\infty(S;\lambda)$ for ion transport also biases the long-time distribution of flow states. Symmetric drive (AC) is converted into directional flow because the invariant measure under λ weights one flow direction more than the other.

1.8 Energy conversion from fluctuating signals (zero-mean noise to net current)

Constraint. Asymmetric conical nanopores in polymer membranes; rectification of ion current.

Phenomenon. An external electrical signal with zero time average (e.g. white noise) is applied across the membrane; the asymmetric pore rectifies it so that a *net* ionic current flows and an external capacitor can be charged to about 1 V within minutes.

Reference. Ramirez et al. [6] (Nano Energy): energy conversion from fluctuating signals using asymmetric nanopores; single-nanopore and multipore membranes; capacitor charging to $\sim$1 V. Gomez et al. [7] (Sci. Rep.): charging a capacitor from an external fluctuating potential using a single conical nanopore.

Interpretation. The constraint λ makes the system's response to positive and negative biases statistically different; the long-time distribution of charge transfer is no longer symmetric under sign flip of the drive. Zero-mean input is converted into net directed transport—a form of "fish gathering" where fluctuations are harvested by the asymmetric λ.

1.9 Osmotic power (blue energy) from salinity gradients

Constraint. Charged asymmetric or structured nanopore membranes separating solutions of different salinity (e.g. seawater vs. freshwater).

Phenomenon. A salt concentration gradient across the membrane drives spontaneous ion selectivity and net ion flux, generating a potential difference and usable electrical power ("blue energy"). Power densities on the order of 0.1–1 $\mathrm{W/m^2}$ have been reported; scaling to multipore membranes and coupling between channels are studied.

Reference. Tsutsui et al. [8] (Osaka Univ., Univ. Tokyo, AIST): scalability of nanopore osmotic energy conversion; role of electrostatic inter-channel coupling in multi-nanopore membranes.

Interpretation. Boundary conditions (salinity gradient) and pore geometry/charge form the constraint λ. The steady state is a non-equilibrium state with persistent current and voltage; $P_\infty(S;\lambda)$ has substantial weight in configurations corresponding to directed ion flow and separation, consistent with constraint-reshaped entropy distributions.

1.10 Nonequilibrium 1/f noise in rectifying nanopores

Constraint. Conical (asymmetric) nanopores with rectifying I–V behaviour.

Phenomenon. Ion current fluctuations show voltage-dependent 1/f noise. Reversing the voltage polarity switches the system between a regime with equilibrium-like noise and one with strong nonequilibrium 1/f noise; the nonequilibrium branch (high-conductance state) shows exponential dependence of the normalized power spectrum on voltage. Ohmic (symmetric) pores do not show this asymmetry.

Reference. Powell, Vlassiouk, Martens, and Siwy [9] (Oak Ridge, UC Irvine): single conical rectifying nanopore; equilibrium vs. nonequilibrium 1/f noise controlled by voltage polarity.

Interpretation. Under one polarity the system samples a region of phase space where the invariant measure gives equilibrium-like fluctuations; under the other, the constraint λ places the long-time state in a regime with distinctly non-equilibrium fluctuations. The same pore thus exhibits two different effective $P_\infty(S;\lambda)$-like behaviours depending on the applied field, illustrating how constraints and boundary conditions shape not only the mean current but the fluctuation spectrum.

1.11 Muddy water: spontaneous sedimentation

Constraint. Gravity and container walls (force field and geometry).

Phenomenon. A well-mixed suspension of mud and water spontaneously separates into clear water and settled sediment over time.

Reference. Standard example of sedimentation; see e.g. Callen [1] (thermodynamics and entropy); Pathria and Beale [2] (statistical mechanics).

Interpretation. Under the given constraints (gravity, boundaries), the long-time distribution $P_\infty(S;\lambda)$ assigns substantial weight to configurations that are more ordered (less mixed) in the coarse-grained sense. Entropy can decrease along typical trajectories; there is no universal "entropy does not decrease" law—only a constraint-dependent distribution.

1.12 Spontaneous phase separation

Constraint. Intermolecular interactions and dynamical boundary conditions.

Phenomenon. A uniform mixture (e.g. oil and water) spontaneously evolves into two distinct phases; local order increases.

Reference. Standard equilibrium and non-equilibrium statistical mechanics; e.g. Callen [1], Pathria and Beale [2].

Interpretation. The constraints λ (interactions, boundaries) define the accessible phase space and the invariant measure. $P_\infty(S;\lambda)$ can have most of its weight in macrostates corresponding to phase-separated (lower mixing entropy) configurations. Spontaneous demixing is consistent with entropy as a stochastic variable whose distribution is reshaped by λ.

1.13 Asymmetric nanopore electrolyte cell: EMF without applied voltage

Constraint. Asymmetric geometry changes ion transit rates and equilibrium distribution.

Phenomenon. In the absence of an applied voltage, cations and anions spontaneously form a concentration gradient and an electromotive force (EMF) is generated.

Reference. Qiao and Wang [3] (concentration gradient and potential in charged small nanopores). Related mechanisms: diffusio-osmosis and asymmetry-driven ion transport in nanopores.

Interpretation. The asymmetric constraint λ reshapes $\mathcal{A}(\lambda)$ and hence $P_\infty(S;\lambda)$. The steady state is a non-equilibrium steady state with a persistent concentration gradient and EMF; the system spontaneously occupies lower-entropy (more ordered) configurations compatible with λ, without requiring compensating entropy increase elsewhere.

1.14 "Fish gathering": harvesting from low-entropy fluctuations

Constraint. Design of constraints (methods/design) to manipulate the long-time distribution.

Phenomenon. By choosing λ so that $P_\infty(S;\lambda)$ has high weight in a low-entropy region, one can "harvest" energy or matter when the system fluctuates into that region ("fish gather").

Reference. Conceptual within the framework of entropy.tex and the FAQ (fish metaphor); no single experiment—rather the design principle implied by constraint-reshaped $P_\infty(S;\lambda)$.

Interpretation. Entropy is a stochastic variable; we do not impose a law that it must increase. By prearranged intervention (choice of λ), we can make the long-time distribution concentrate in favourable (e.g. low-entropy) ranges and exploit fluctuations for energy conversion or separation. The preceding cases are concrete realisations from multiple research groups; "fish gathering" is the general strategy of using constraint design to steer $P_\infty(S;\lambda)$ for practical use.

1.15 Entropy decrease in an isolated system: molecular-sized gate (locally nonchaotic barrier)

Constraint. A locally nonchaotic barrier—a nanoporous membrane one-sidedly surface-grafted with bendable organic chains that act as a "molecular-sized outward-swinging gate." The gate interrupts the local probability distribution of microstates and imposes additional constraints on the global accessible states.

Phenomenon. In an isolated system, gas spontaneously and repeatedly flows from the *low*-pressure side to the *high*-pressure side through the membrane. The crossing probability is asymmetric under local nonchaoticity. The authors show that entropy can decrease in the isolated system and that useful work may be produced in a cycle from a single thermal reservoir; the mechanism is distinct from Maxwell's demon and Feynman's ratchet and is consistent with microscopic reversibility.

Reference. Qiao, Shang, and Kou [11]: experiment and theory of a locally nonchaotic barrier; Phys. Rev. E **104**, 064133 (2021); arXiv:2106.06648.

Interpretation. The gate geometry and the one-sided grafting constitute the constraint λ, which reshapes the accessible phase space and the long-time measure. $P_\infty(S;\lambda)$ is concentrated in configurations where the gas has moved against the pressure gradient; spontaneous entropy decrease and "reverse" flow are direct consequences of constraint-reshaped distributions, without invoking a universal "entropy does not decrease" law. This experiment is a close relative of the Qiao–Wang nanopore work and fits the same theoretical framework.

1.16 Spontaneous particle ordering, sorting, and assembly on soap films

Constraint. Soap film (two liquid–gas interfaces) with a balance of interfacial tensions; particle–interface coupling depends on particle size and hydrophilicity. The film geometry and the paths defined by the tension balance act as the constraint.

Phenomenon. Without external energy input, "belted wetted particles" (BWPs) spontaneously travel along specified paths on the soap film. Path selection depends on particle size and hydrophilic properties, enabling spontaneous particle *sorting* via distinct paths for different particles. Deformation of the soap membrane facilitates 1D and 2D particle organisation along these paths, realising energy-free particle separation and soft colloidal crystal assembly.

Reference. Shi et al. [12], *Nano Lett.* (2024): first observation of spontaneous particle ordering on soap films; DOI 10.1021/acs.nanolett.4c01840; Jinan Univ., UC Berkeley, and collaborators.

Interpretation. The constraint λ (soap film geometry, two interfaces, size/hydrophilicity-dependent coupling) defines the effective dynamics and the long-time distribution of particle positions. $P_\infty(S;\lambda)$ has high weight in ordered, sorted configurations (particles along paths, separated by type). Spontaneous order and separation are again consequences of the constraint-reshaped distribution, not of a universal entropy-increase law.

1.17 Chirality-induced phase separation in binary mixtures of chiral active particles

Constraint. Activity and chirality of the particles (and, in the numerical study, boundary and packing conditions). The dynamical rules—chiral active motion—and the chirality ratio between the two species act as the constraint parameters λ.

Phenomenon. Binary mixtures of chiral active particles with different chiralities spontaneously phase-separate *without* attractive forces between particles. "Chirality-induced nonhomogeneous bubble phases" cluster similar particles; the chirality ratio, reduced inertial time, and packing fraction determine the separation efficiency. Particles with the same chirality direction but different magnitudes can achieve strong separation; opposite chiralities yield different collective structures.

Reference. Guo, Li, and Ai [13] (South China Normal University), *Phys. Rev. E* **111**, 045423 (2025): chirality-induced phase separation and collective dynamics in binary mixtures of chiral particles (numerical study).

Interpretation. Activity and chirality define the effective constraint λ on the phase-space exploration of the system. Under this λ, the long-time distribution $P_\infty(S;\lambda)$ places substantial weight on phase-separated (lower mixing entropy) configurations. Spontaneous demixing is a statistical consequence of the constraint-reshaped distribution, consistent with "entropy has no direction" and with the same framework as sedimentation and equilibrium phase separation, now extended to active matter.

2 Summary table

Table 1 summarises all 17 cases: constraint type, main observation, and reference.

Summary and implications

These 17 cross-disciplinary experiments and numerical studies form a complementary empirical matrix that systematically validates the universality of the "constraints reshape the entropy distribution" theory. The observations clearly show that spontaneous order arises not only at the microscopic nanoscale—in ion lineups and charge enrichment—but also in macroscopic classical systems such as sedimentation and phase separation, and in soft-matter and active-matter systems (soap films, chiral active particles). Key evidence indicates that when the constraint parameters λ (including geometry, potential fields, boundary conditions, and activity rules) break the translational symmetry of phase space, the long-time measure of the system undergoes a structural shift. In particular, the "over-limit voltage" and "work in an isothermal cycle" observed in the Qiao–Wang experiment, and the spontaneous gas flow from low to high pressure in the Qiao–Shang–Kou molecular gate experiment, directly challenge the traditional thermodynamic dogma that "work conversion from a single heat reservoir is impossible." These phenomena demonstrate that spontaneous access to low-entropy states is not a rare "random fluctuation" but a statistical necessity once the distribution is reshaped by the appropriate constraints. Furthermore, the experiments of Ramirez, Gomez, and coworkers, which use asymmetric geometry to convert a zero-mean noise signal into electrical energy at about 1 V, strongly refute the old assumption that "local order must be compensated by the environment." The consistency of the evidence across physics, chemistry, energy conversion, signal processing, and soft/active matter shows that "entropy has no direction" is not only a logically rigorous theoretical result but a physical fact grounded in first principles and repeatedly validated under a variety of constraints—and one that can be engineered.

Table 1: Summary of the 17 cases: constraint, phenomenon, and reference.

#	Case	Constraint	Key observation	Reference
1	Ion lineups (quasi-1D)	$d_e \approx d_i$, geometry	Ions form lineups; no full relaxation	Qiao–Wang
2	Voltage exceeding 2nd law	Charged asym. nanopores	$\lvert\delta V\rvert$ ∼1 order above heat-engine limit	Qiao–Wang
3	SND	Local asym. energy barriers	$S < S_{\mathrm{eq}}$; NESS under constraint	Qiao–Wang
4	Non-Boltzmann enrichment	Geometry → $\mathcal{A}(\lambda)$	$\sigma^{\pm}$ deviates from Boltzmann	Qiao–Wang
5	Work from single reservoir	Asymmetric constraint	Isothermal cycle: heat in → work out	Qiao–Wang
6	Geometric rectification	Asym. nanopore/channel	Diode-like I–V; directional migration	Siwy; Experton et al.
7	EOF rectification & AC pump	Asym. pore + permselectivity	AC voltage → net flow	Experton, Wu, Martin
8	Fluct. signal → net current	Asym. conical pore	Zero-mean noise → cap. ∼1 V	Ramirez; Gomez et al.
9	Osmotic power (blue energy)	Membrane + salinity gradient	Spontaneous EMF & power	Tsutsui et al.
10	Nonequil. 1/f noise	Conical rectifying pore	Polarity: equil. vs. nonequil. noise	Powell, Vlassiouk, Siwy
11	Muddy water sedimentation	Gravity + walls	Spontaneous separation: clear + sediment	Callen; Pathria
12	Phase separation	Interactions + boundaries	Uniform → two phases (e.g. oil–water)	Callen; Pathria
13	EMF without applied V	Asymmetric geometry	Spontaneous concentration gradient & EMF	Qiao–Wang
14	"Fish gathering"	Design of λ	Harvest when P_∞ weights low-S	Conceptual
15	Entropy decrease (isolated)	Locally non-chaotic gate	Gas: low → high pressure; single-reservoir work	Qiao, Shang, Kou
16	Particle ordering on soap films	Soap film + interfacial tension	Spontaneous paths, sorting, 1D/2D assembly	Shi et al.
17	Chiral active phase separation	Activity + chirality	Binary mixture demixes without attraction	Guo, Li, Ai

References

[1] H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics* (Wiley, 2nd ed., 1985).

[2] R. K. Pathria and P. D. Beale, *Statistical Mechanics* (Elsevier, 3rd ed., 2011).

[3] Y. Qiao and M. Wang, "Breaking the boundaries of the second law of thermodynamics: Intrinsic nonequilibrium distribution of large ions in charged small nanopores," arXiv:2407.04599 [cond-mat.soft] (2025).

[4] Z. S. Siwy, "Ion-current rectification in nanopores and nanotubes with broken symmetry," *Adv. Funct. Mater.* **16**(6), 735–746 (2006).

[5] J. Experton, X. Wu, and C. R. Martin, "From ion current to electroosmotic flow rectification in asymmetric nanopore membranes," *Nanomaterials* **7**(12), 445 (2017).

[6] P. Ramirez, P. Gomez, J. Cervera, S. Nasir, M. Ali, W. Ensinger, and S. Mafe, "Energy conversion from external fluctuating signals based on asymmetric nanopores," *Nano Energy* **16**, 375–382 (2015).

[7] V. Gomez, P. Ramirez, J. Cervera, S. Nasir, M. Ali, W. Ensinger, and S. Mafe, "Charging a capacitor from an external fluctuating potential using a single conical nanopore," *Sci. Rep.* **5**, 9501 (2015).

[8] M. Tsutsui, W.-L. Hsu, K. Yokota, I. W. Leong, H. Daiguji, and T. Kawai, "Scalability of nanopore osmotic energy conversion," *Exploration* **4**(2), 20220110 (2024).

[9] M. R. Powell, I. Vlassiouk, C. Martens, and Z. S. Siwy, "Nonequilibrium 1/f noise in rectifying nanopores," *Phys. Rev. Lett.* **103**, 248104 (2009).

[10] Y. Zhou, X. Liao, J. Han, T. Chen, and C. Wang, "Ionic current rectification in asymmetric nanofluidic devices," *Chinese Chem. Lett.* **31**(9), 2414–2422 (2020).

[11] Y. Qiao, Z. Shang, and R. Kou, "Molecular-sized outward-swinging gate: Experiment and theoretical analysis of a locally nonchaotic barrier," *Phys. Rev. E* **104**, 064133 (2021); arXiv:2106.06648.

[12] X. Shi et al., "Spontaneous particle ordering, sorting, and assembly on soap films," *Nano Lett.* (2024); DOI: 10.1021/acs.nanolett.4c01840.

[13] R.-X. Guo, J.-J. Li, and B.-Q. Ai, "Chirality-induced phase separation and collective dynamics in binary mixtures of chiral particles," *Phys. Rev. E* **111**, 045423 (2025).