Thermodynamics and Phase Coexistence in Nonequilibrium Steady States

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Equilibrium　　　*Nonequilibrium*

Nonequilibrium steady state (NESS):

Macroscopic properties are time-independent

But there is a steady **current** (of particles, energy,...)

Focus on far-from-equilibrium systems

NESS is closest analog to equilibrium, in far-from-equilibrium context

NESS

Key questions:

Is there a thermodynamics of nonequilibrium steady states?

What is a nonequilibrium phase?

Is there a nonequilibrium entropy?

OUTLINE

I. Steady-state thermodynamics (SST)

Definition of intensive variables (chemical potential and temperature) via *coexistence with a reservoir*

Works in spatially uniform systems if we use *Sasa-Tasaki transition rates* (otherwise, zeroth-law violations)

Fails in nonuniform systems

II. Phase coexistence of NESS

Phase coexistence ill-defined, SST doesn't predict coexisting phases

III. Nonequilibrium entropy is not the Shannon entropy

SST originally proposed in

Y. Oono and M. Paniconi, Prog. Th. Phys. Supp. **130**, 29 (1998)

A detailed proposal with applications to lattice gases:

S. Sasa and H. Tasaki, J. Stat. Phys. **125**, 125 (2006)

Numerical test of zeroth law in KLS driven lattice gas:

P. Pradhan, R. Ramsperger, and U. Seifert, Phys. Rev. E**84**, 041104 (2011)

Easiest case: spatially uniform, athermal (only excluded-volume interactions)

In athermal systems the only intensive parameter is the dimensionless chemical potential, $\mu^* = \mu/k_BT$

Criteria for a valid chemical potential:

1) (Zeroth law) If systems A and B coexist, and A and C coexist, then B and C must also coexist

2) Suppose systems A and B, initially isolated, with $\mu^*_A \neq \mu^*_B$.

If they are allowed to exchange particles, the ensuing flux should act to **equalize** their chemical potentials.

Knowing $\mu^*_A(\rho)$ and $\mu^*_B(\rho)$ should allow us to **predict** the final densities when the systems are allowed to exchange particles.

Coexistence of NESS

Consider systems A and B in steady states (equilibrium or not)

If A and B can exchange particles, and the net particle flux between them is zero, we say they coexist wrt particle exchange; we declare them to have the same value of μ^*

Analogous definition of temperature for coexistence wrt energy exchange

If B is a **particle reservoir** of known chemical potential the zero-flux condition defines the chemical potential of A

What is a reservoir?

- A system large enough that its intensive properties don't vary under exchange of particles and/or energy

- Internal structure irrelevant

- The reservoir doesn't "know" what kind of system it's in contact with, in particular, whether this system is in equilibrium or not.

A **particle reservoir** R in contact with an athermal lattice gas A attempts to insert particles into, and remove particles from A, with rates p_I and p_R, respectively. In insertion attempt is successful if the selected site is free to be occupied; a removal attempt is successful if the selected site is occupied.

From equilibrium statistical mechanics we know $p_I/p_R = e^{\mu^*}$

$\mu*$ is a property of the **reservoir**

## Application to driven lattice gas with nearest-neighbor exclusion (NNE)

Each particle excludes nearest-neighbor sites – hard-core repulsive potential

Equilibrium dynamics: symmetric nearest-neighbor hopping attempts

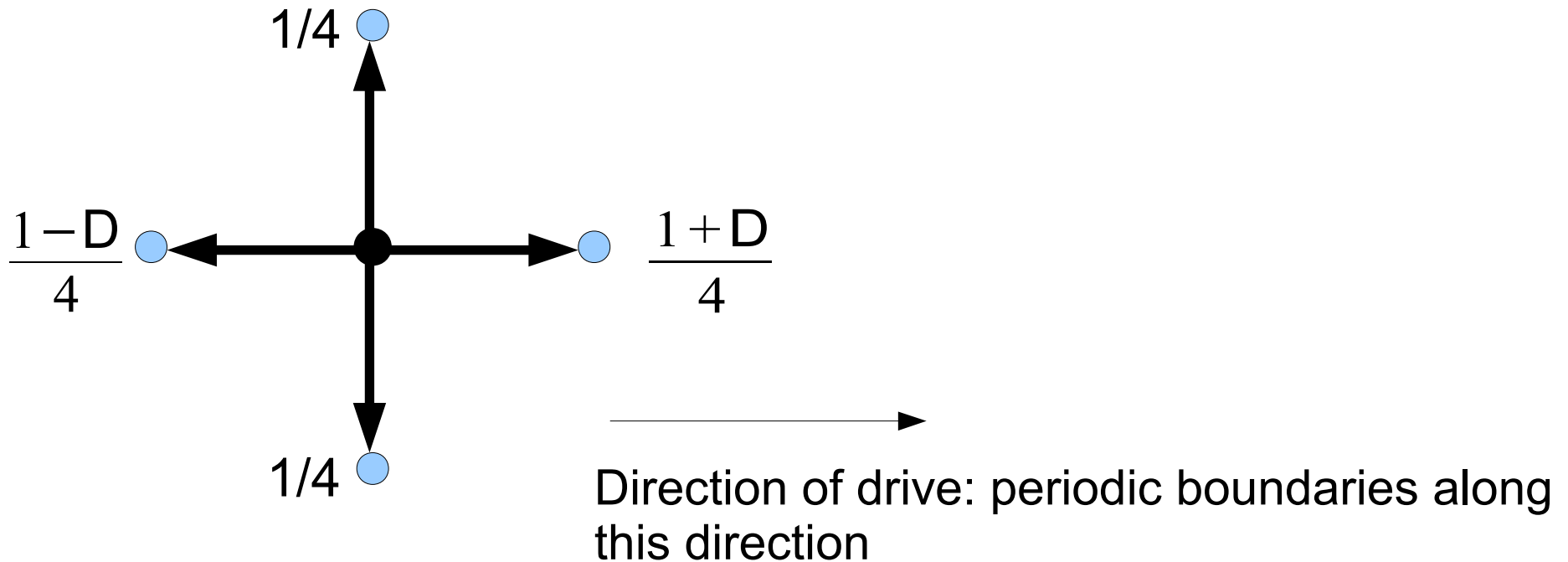Nonequilibrium (driven) dynamics: preferred hopping direction

Can include hopping to second-neighbor sites to maintain ergodicity at higher densities

NNE Lattice Gas
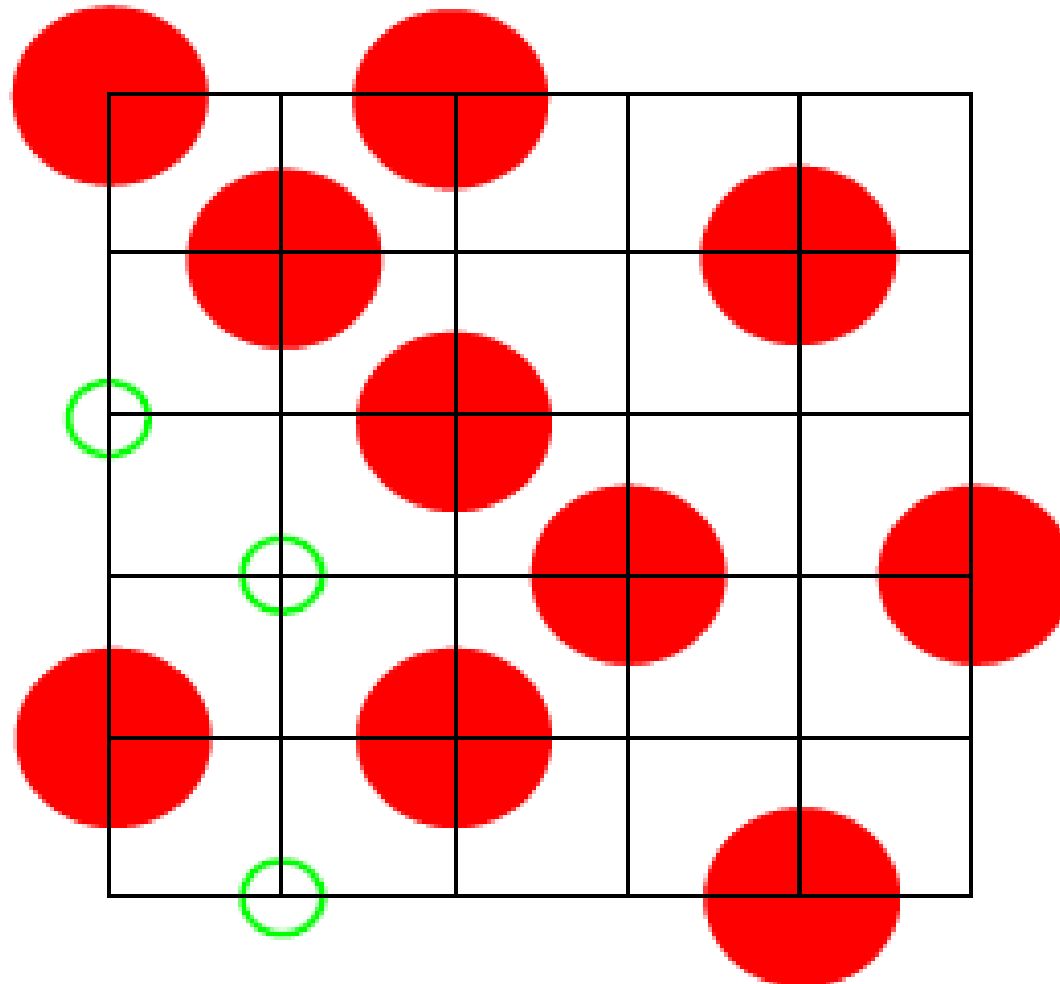
Red: occupied; green: open

NNE Lattice Gas on square lattice: hopping probabilities for nearest-neighbor dynamics

$\dfrac{1}{4}$

$\dfrac{1-D}{4}$ $\dfrac{1+D}{4}$

$\dfrac{1}{4}$

Direction of drive: periodic boundaries along this direction

For D=0 the dynamics obeys detailed balance and the stationary distribution is that of equilibrium

D ≠ 0 represents nonequilibrium: the is a current along drive
D=1: maximum drive

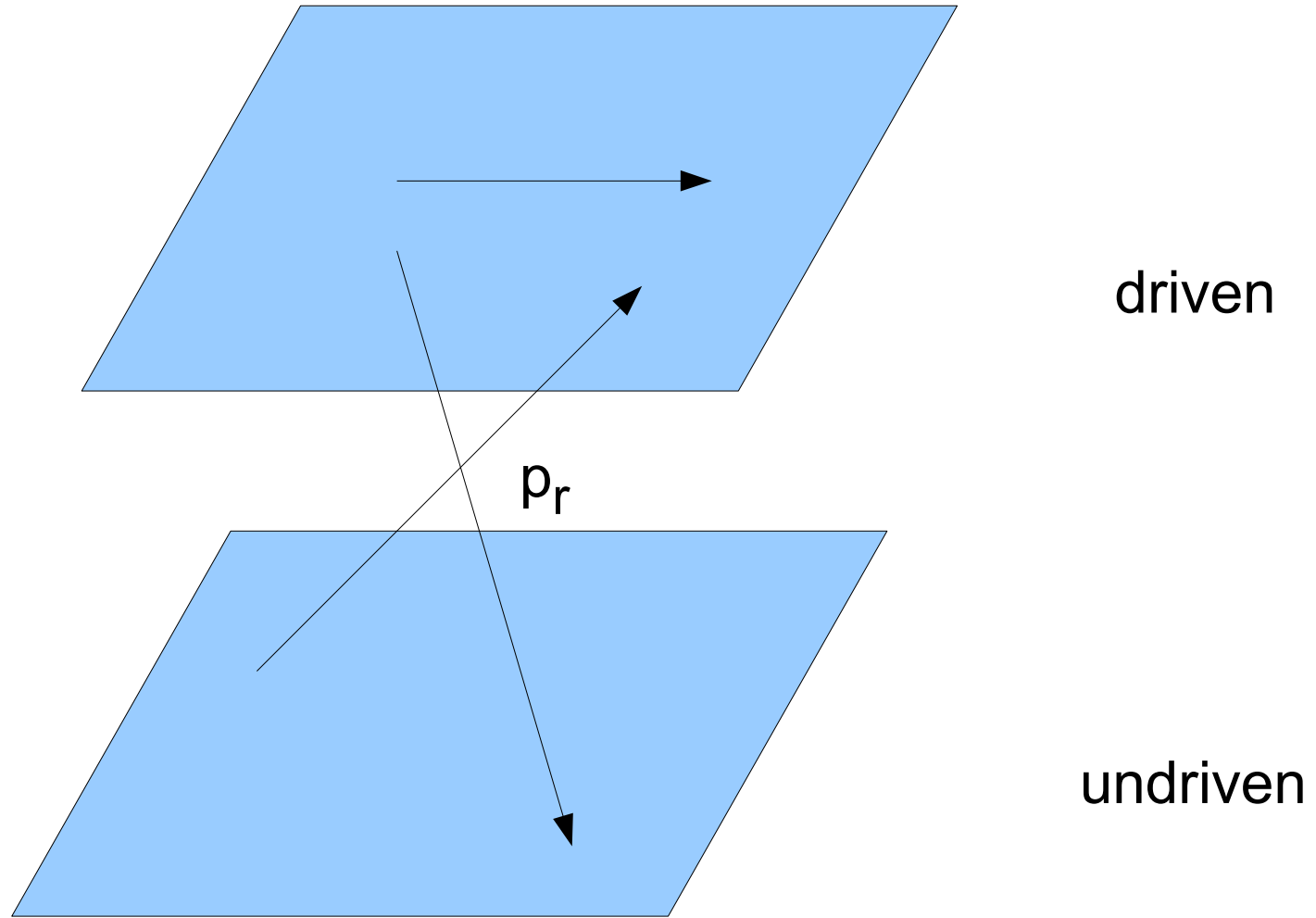NNE lattice gas and other athermal systems: chemical potential given by

$$\mu* = \ln (\rho / \rho_{op})$$

where ρ_{op} is the density of open sites (sites at which particles may be inserted)

This follows from the condition of coexistence with the particle reservoir:

$$\rho \, p_R = \rho_{op} \, p_I$$

and the relation $p_I / p_R = e^{\mu*}$

driven

p_r

undriven

Global exchange between driven and undriven systems
Weak exchange limit $p_r \to 0$

Obs: Global exchange not strictly necessary;
weak exchange *is*

Zeroth law:

If systems A and B both coexist with the same reservoir, they must coexist with one another

The zeroth law is satisfied under weak, global exchange: the net particle flux between two systems A and B is proportional to

$$\rho_A \, \rho_{op,B} - \rho_B \, \rho_{op,A} \, ,$$

which is zero if $\mu^*_A = \mu^*_B$

Note that we treat the systems as *independent*, which implies an exchange rate tending to zero ("weak" exchange)
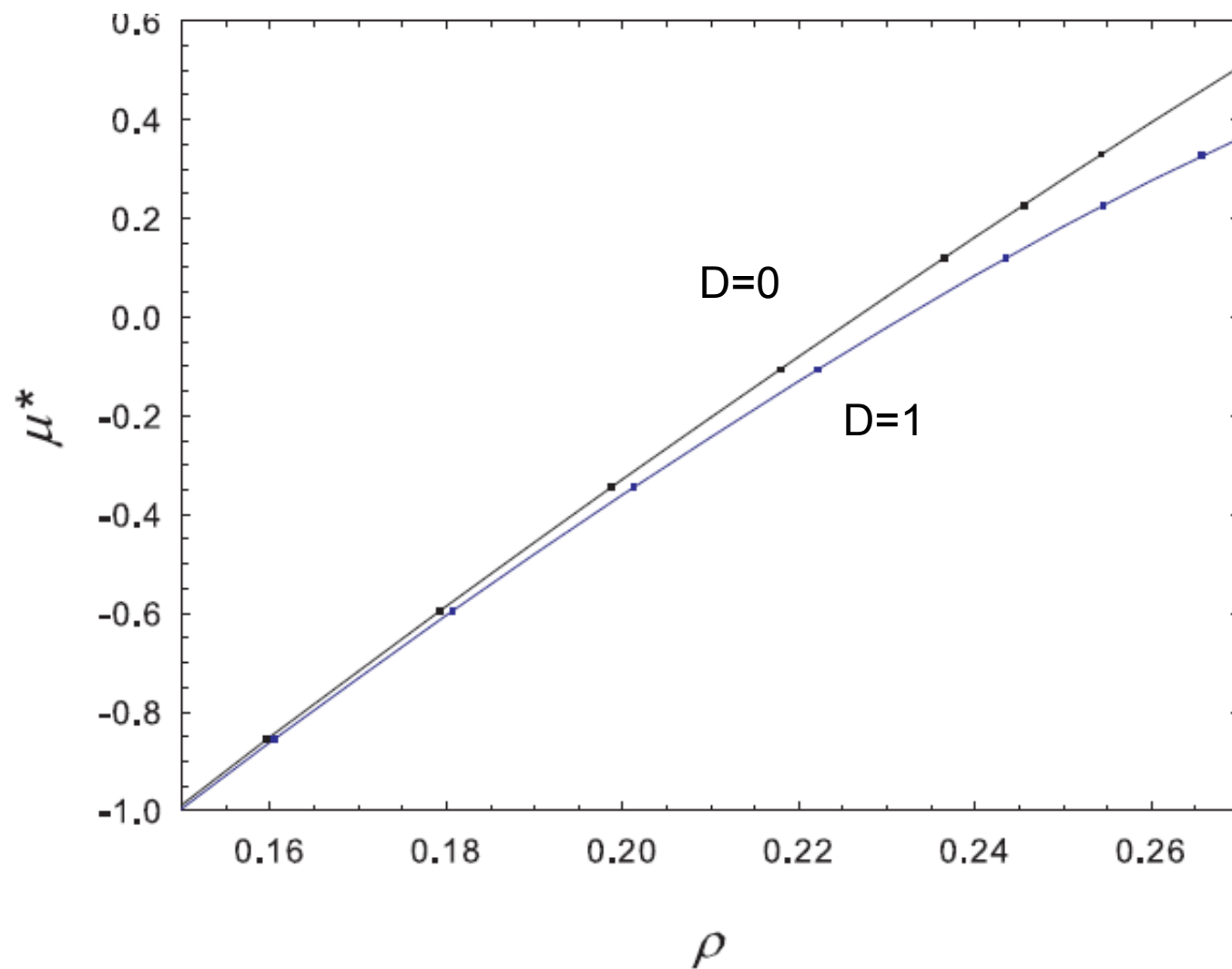
Chemical potential of NNE lattice gas

FIG. 1: NNE lattice gas: simulation results for μ^* in equilibrium (black curve) and under maximum drive (blue curve), system size $L = 80$. Pairs of points sharing the same value of μ^* represent coexisting densities in the equilibrium and driven systems under weak exchange. Uncertainties are smaller than line thickness and symbol size.
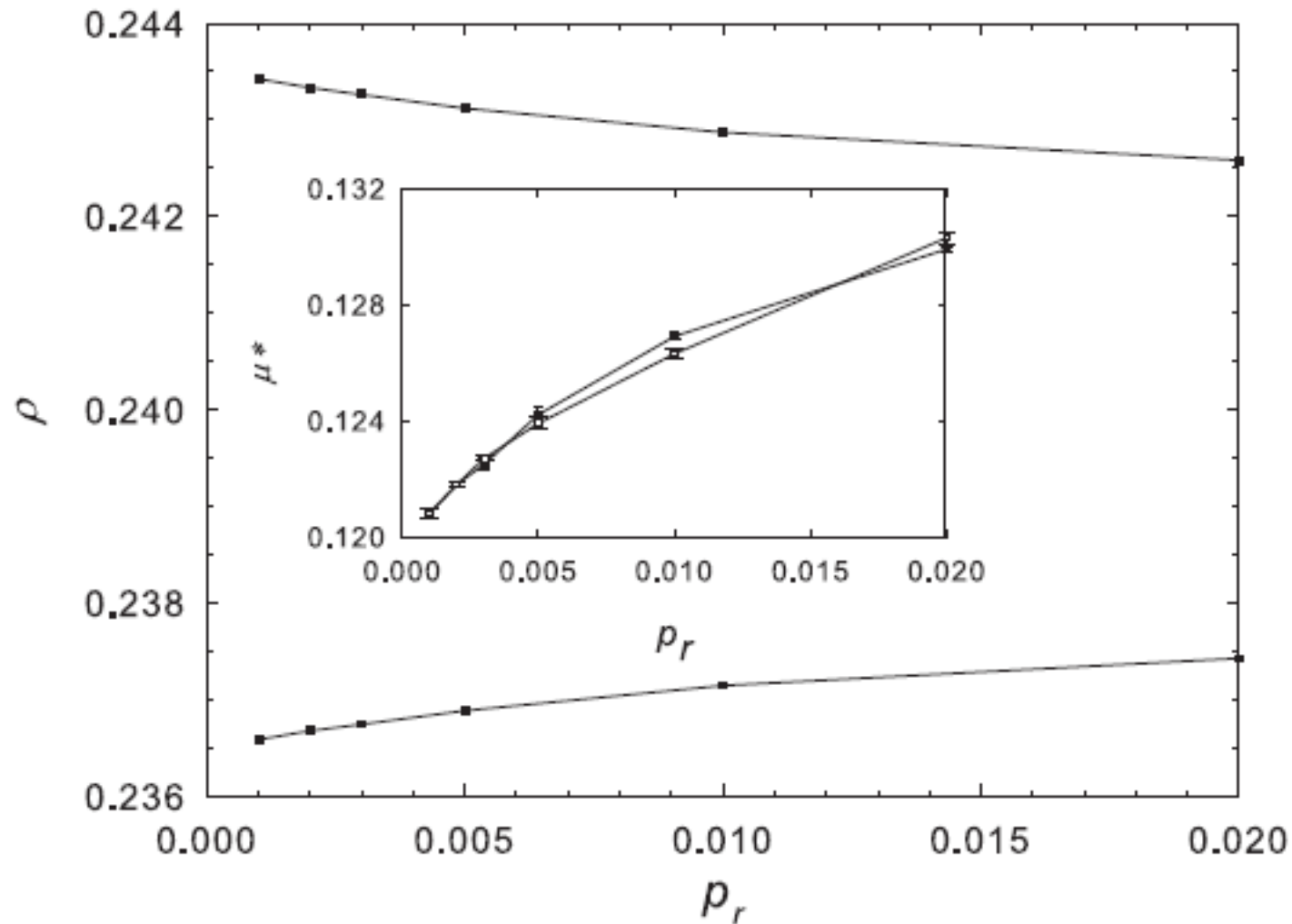
NNE lattice gas: weak-exchange limit

FIG. 2. NNE lattice gas: simulation results for coexisting densities in a nondriven system (lower) and under maximum drive (upper) as a function of exchange rate p_r (system size $L = 80$; mean density $\overline{\rho} = 0.24$). Inset: chemical potentials μ^* at coexistence (for the same parameters) in the nondriven (squares) and driven ($\times$) systems. Error bars are smaller than symbols.

Driven NNE lattice gas

In the weak-exchange limit, the chemical potential at coexistence corresponds to that of the **isolated** systems at the densities that equalize their μ^* values, subject to the fixed total density.

Since μ^* is an increasing function of density, if NNE models with different values of μ^* are permitted to exchange particles, the ensuing flux will tend to equalize the chemical potential.

Thus μ^* satisfies the minimal conditions for a chemical potential, both in equilibrium and in a NESS.

Driven lattice gas or Katz-Lebowitz-Spohn (KLS) model with attractive nearest-neighbor interactions.

The system evolves via a particle-conserving dynamics with a drive $\mathbf{D} = D\mathbf{i}$ favoring particle displacements along the $+x$ direction and inhibiting those in the opposite sense.
***PBCs along drive!

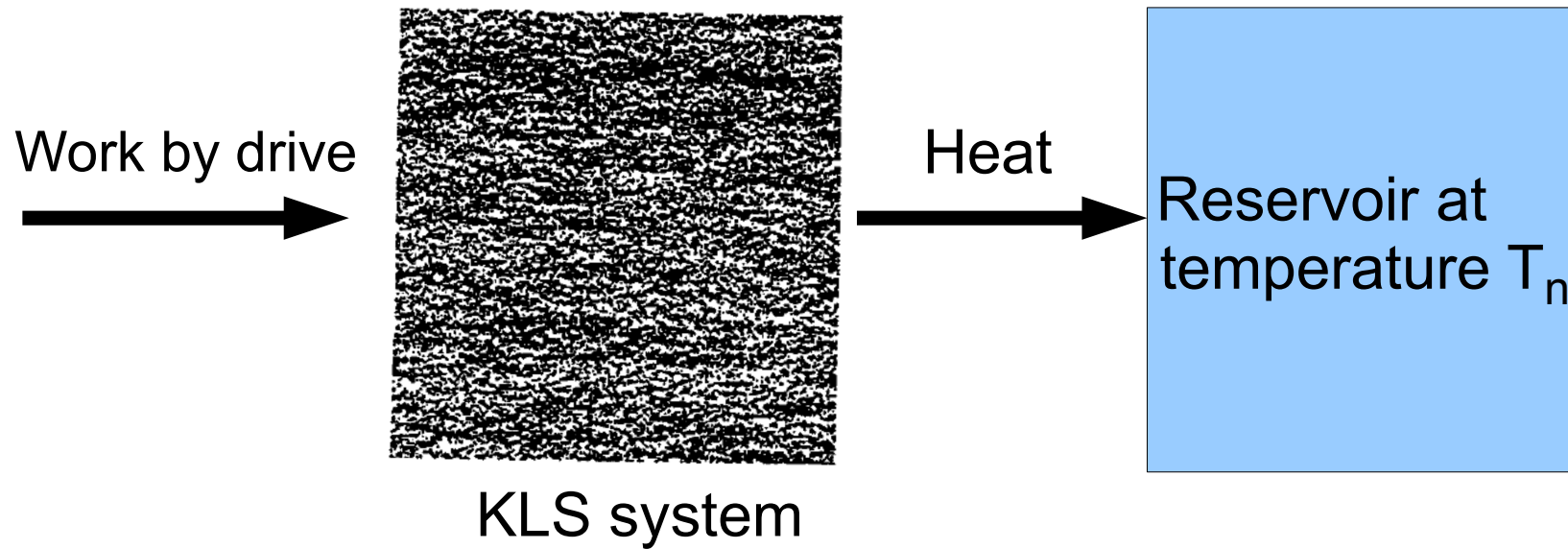Acceptance probability for a particle displacement $\Delta\mathbf{x}$ is

$$p_a = \min\{1,\ \exp[-(\Delta E - \mathbf{D} \cdot \Delta\mathbf{x})/T_R\,]\}$$

Energy of configuration C: $E(C) = -\sum_{<i,j>} \sigma_i \sigma_j$

The σ_j are site occupation variables
T_R is the temperature of the reservoir, but (for $D \neq 0$)
not the temperature of the system

Energy flow though KLS system

Work by drive $\longrightarrow$ Heat $\longrightarrow$ Reservoir at temperature T_n

KLS system

We define the temperature and chemical potential of a KLS system (driven or not) via coexistence with a reservoir **R** of heat and particles

R is a test system used to measure the temperature and chemical potential of the system, *not* the reservoir to which the KLS system rejects heat.

The reservoir T and μ are defined by the usual relations of statistical mechanics. When the KLS system coexists with **R** it shares its values of T and μ.

[In paractice T and μ are determined by measuring certain nearest-neighbor probabilities in simulations of the system; explicit contact with a reservoir is unnecessary to determine the coexistence parameters.]

Let $\mathbf{R}$ be a reservoir with temperature and chemical potential equal to that of a driven KLS system S, and let S_0 be an undriven (equilibrium) nearest-neighbor lattice gas with the same temperature and chemical potential as $\mathbf{R}$ and S.

If the Zeroth Law holds, S and S_0 must coexist. Do they?

No! Although S and S_0 both coexist with $\mathbf{R}$, in general, they do not coexist with each other, violating the zeroth law

The Zeroth Law does hold for Sasa-Tasaki exchange rates between the systems

Numerical studies (simulation and exact solution of master eq) yield the fluxes between S and S_0

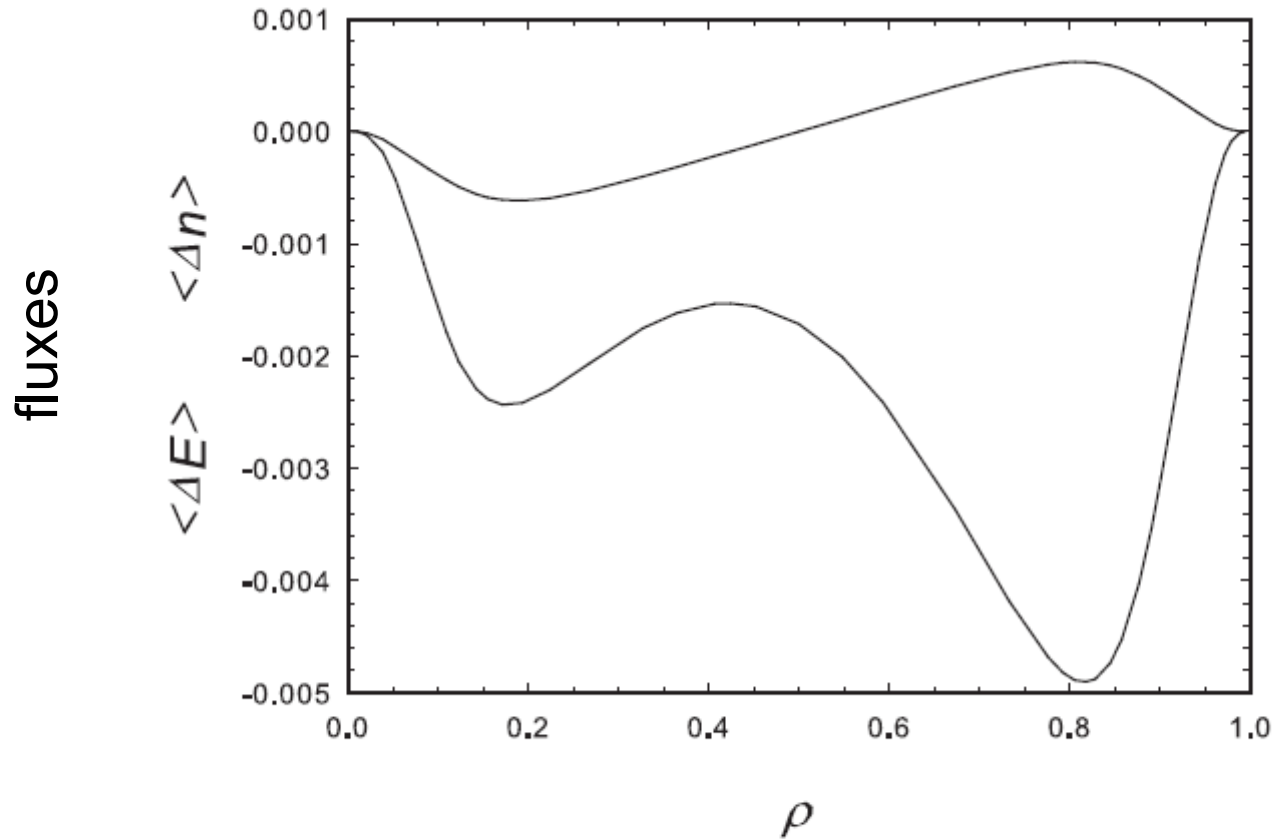# Zeroth law violations under Metropolis exchange rates

FIG. 7: KLS lattice gas: particle flux $\langle \Delta n \rangle_{\mathcal{SS}_0}$ (upper curve) and energy flux $\langle \Delta E \rangle_{\mathcal{SS}_0}$ (lower curve), under virtual exchange, between a driven system $\mathcal{S}$ (nominal temperature $T_n = 0.6$, drive $D = 10$) and an equilibrium system $\mathcal{S}_0$, both of which coexist with the same reservoir. Results obtained via numerical solution of the master equation for systems of 4×4 sites.

Equivalent to a temperature mismatch of ~0.4%

Sasa-Tasaki (ST) rates

The rate for transferring a particle from A to B depends only on the energy change and parameters of A, and vice-versa.

Detailed balance implies the rate of particle transfer from A to B:

$$W_{ST} = \varepsilon \exp\left[-(\mu_A + \Delta E_A)/T_{R,A}\right]$$

and similarly for B to A. (ε is an arbitrary fixed rate.)

Physical picture: rate is determined by energy barrier to activated state, not energy difference between initial and final states, as in, e.g., Metropolis rates

KLS model: Effective temperature and chemical potential under ST exchange (reservoir temperature T_R=1, D=10)
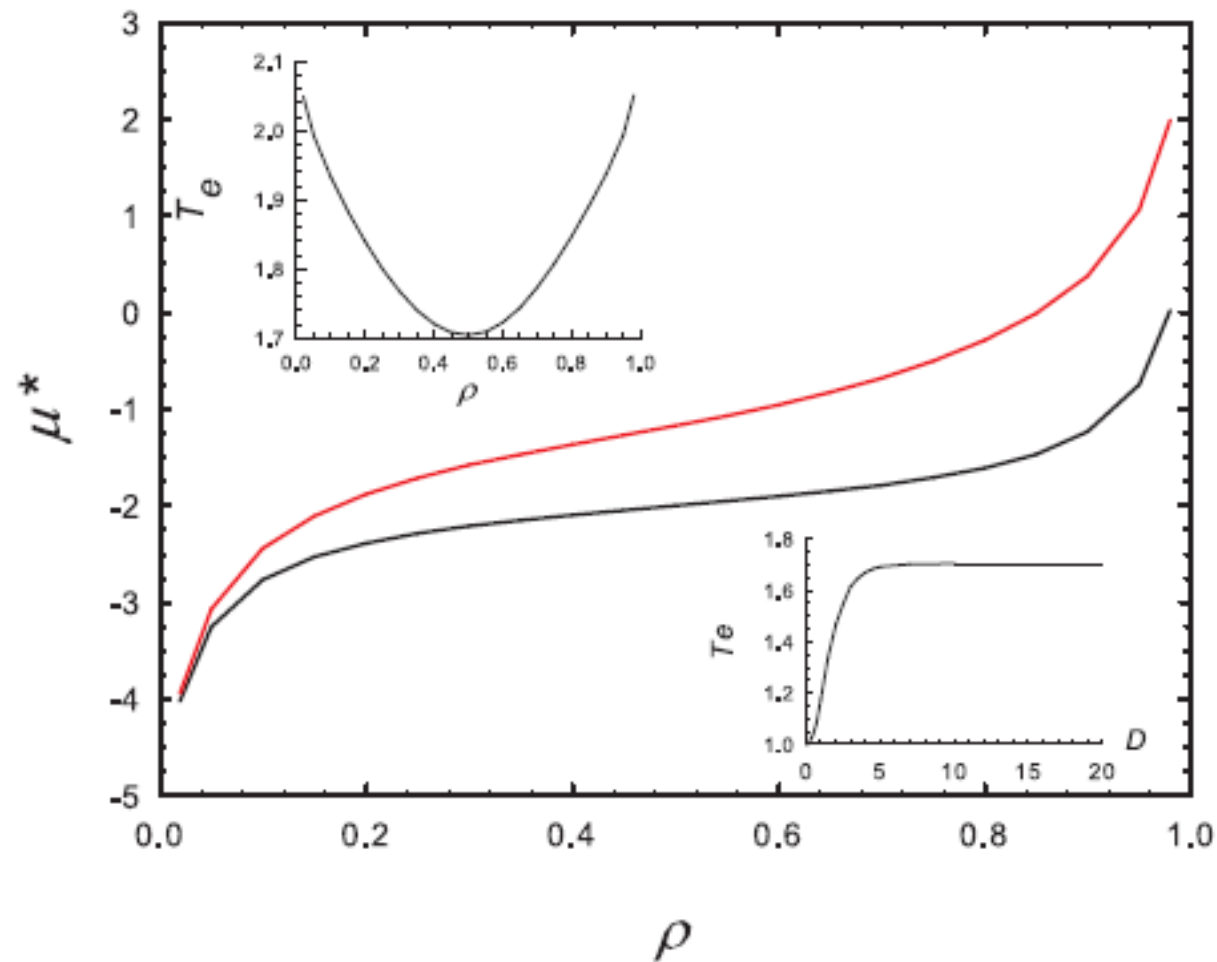

FIG. 8: KLS lattice gas: dimensionless chemical potential μ^* versus density for $T = 1$ in equilibrium (black curve) and effective μ^* for driven lattice gas with $T_n = 1$ and drive $D = 10$. Upper inset: effective temperature T_e of driven system versus density. Lower inset: effective temperature of driven system versus drive D for density $\rho = 0.5$ and $T_n = 1$. System size $L = 80$. Effective parameters for the driven system are obtained using Sasa-Tasaki exchange rates.

Summary of results on **uniform** KLS lattice gas

The intensive parameters T and μ are defined via coexistence with a reservoir **R.**

For drive D>0, T (=T_R) > T_R

Only ST rates permit a consistent definition of intensive parameters for NESS

We appear to have a general scheme for defining the temperature and chemical potential of spatially uniform systems in a NESS

Nonuniform athermal systems

Given the success of steady-state thermodynamics using ST rates, applied to spatially uniform systems, we turn to NESS with nonuniformities provoked by:

- a nonuniform drive

- a wall

- nonuniform time scale

Steady-state thermodynamics *fails* in these cases

Test of SST in half-driven NNE lattice gases (ST rates):
## Can SST predict coexisting densities in a nonuniform system?
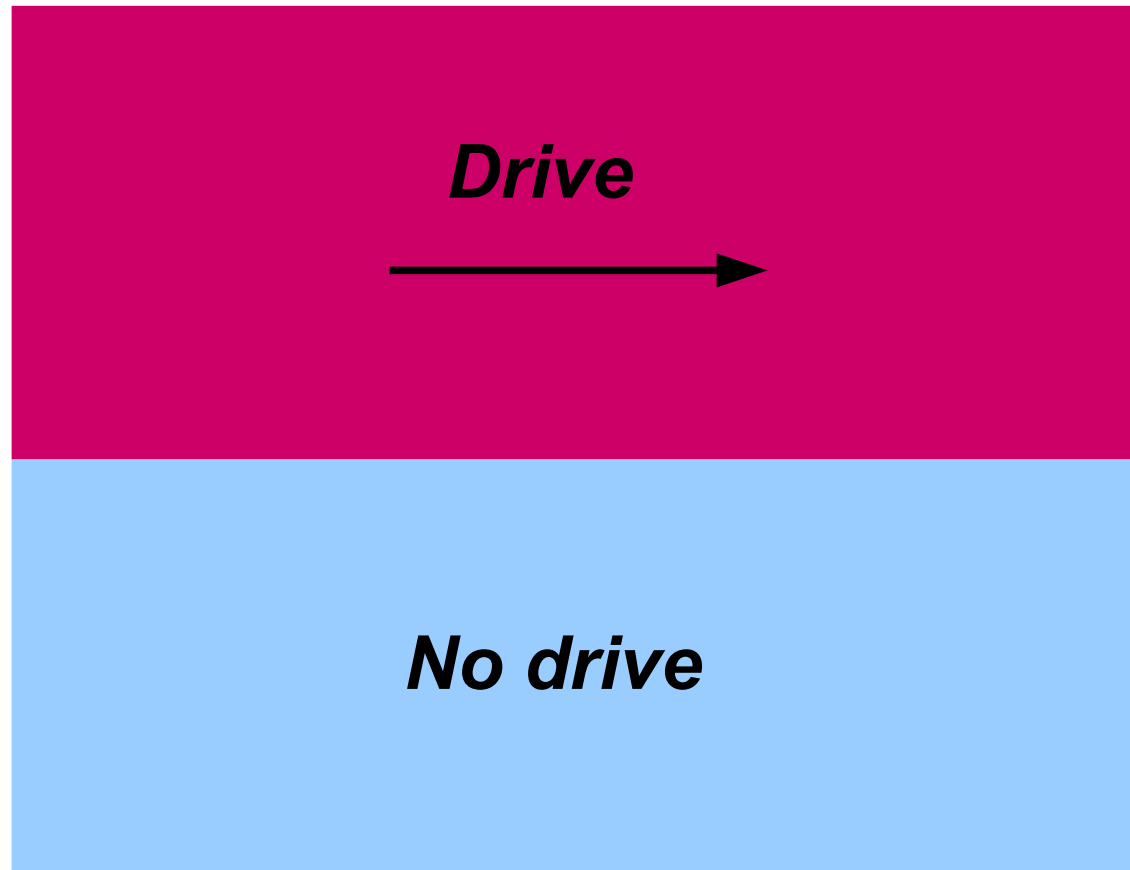
Half-driven NNE model

For the same density, μ^* is smaller in the driven system than without drive.

Equating chemical potentials, the density in the driven region should be larger.

Nevertheless, the particles migrate in the *opposite* sense!

# Stationary density and chemical potential profiles in half-driven NNE
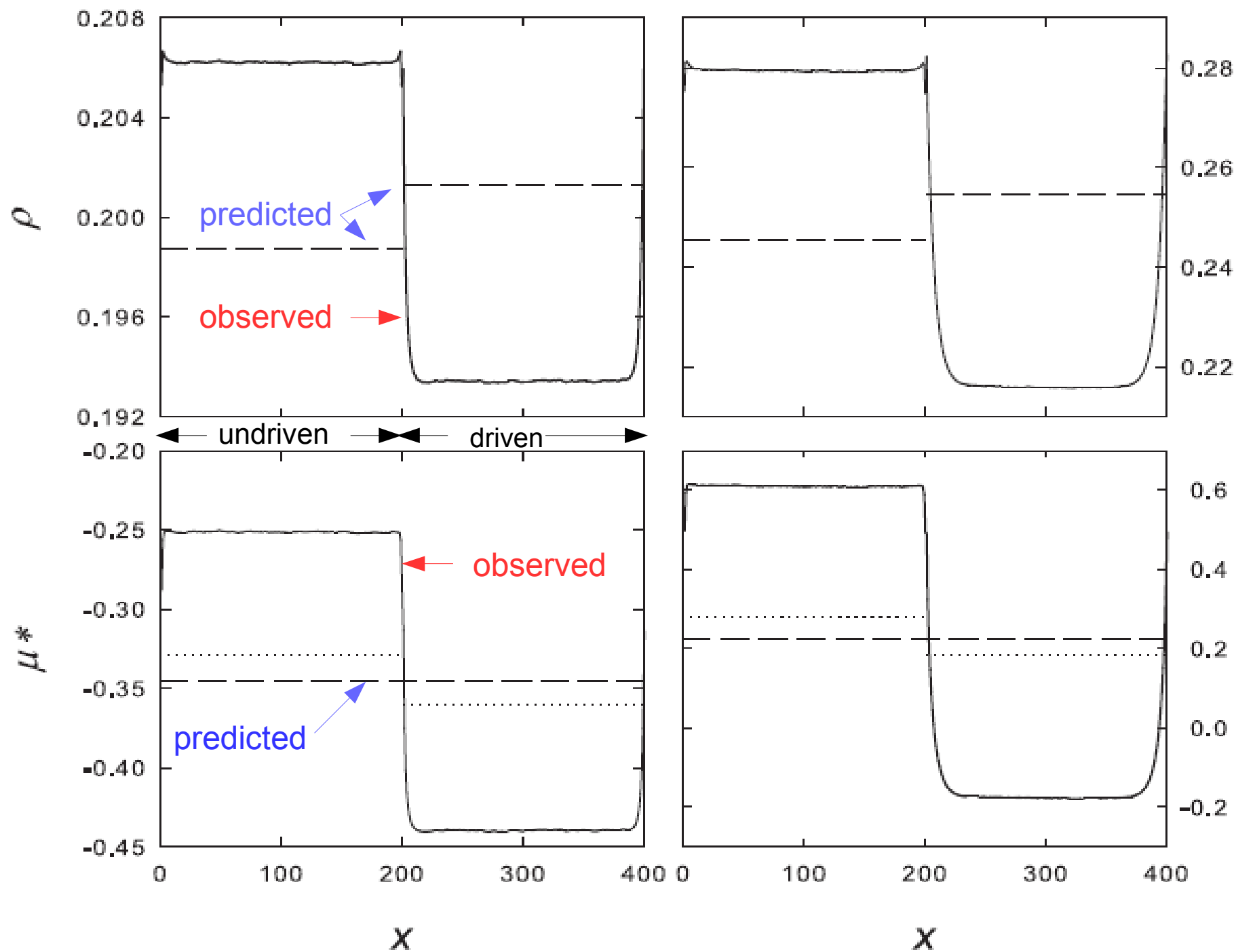
Conclusions (I)

- We appear to have a general scheme for defining the temperature and chemical potential of spatially uniform systems in a NESS

- A pair of systems (driven/undriven) that coexist under weak exchange **don't coexist** when in contact along an edge

- This result **doesn't depend** on whether we define a chemical potential μ

- In half-driven system particles migrate contrary to Fick's law: the final state has a larger μ difference than the initial uniform state

II. Can SST predict the densities of coexisting phases?

KLS model

 - under drive, phase separation into **strips** oriented along drive;

 - use Sasa-Tasaki rates for particle movement perpendiclar to drive: necessary for consistency of SST under coexistence between rows parallel to drive
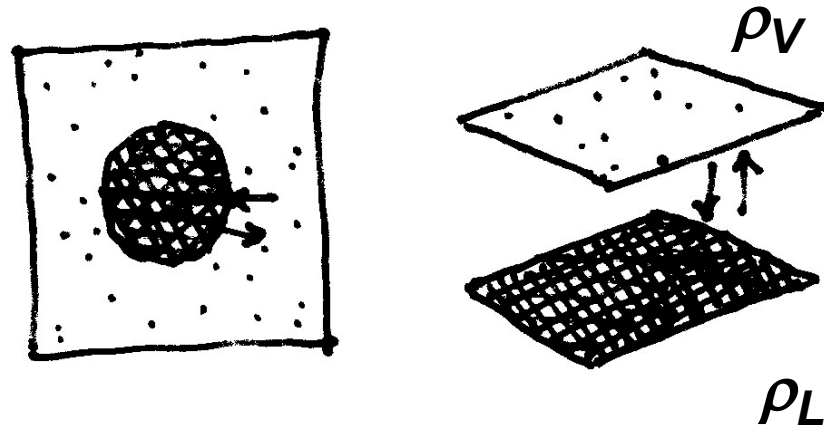
KLS: Typical phase-separated configuration, $T_R = 0.6$
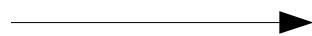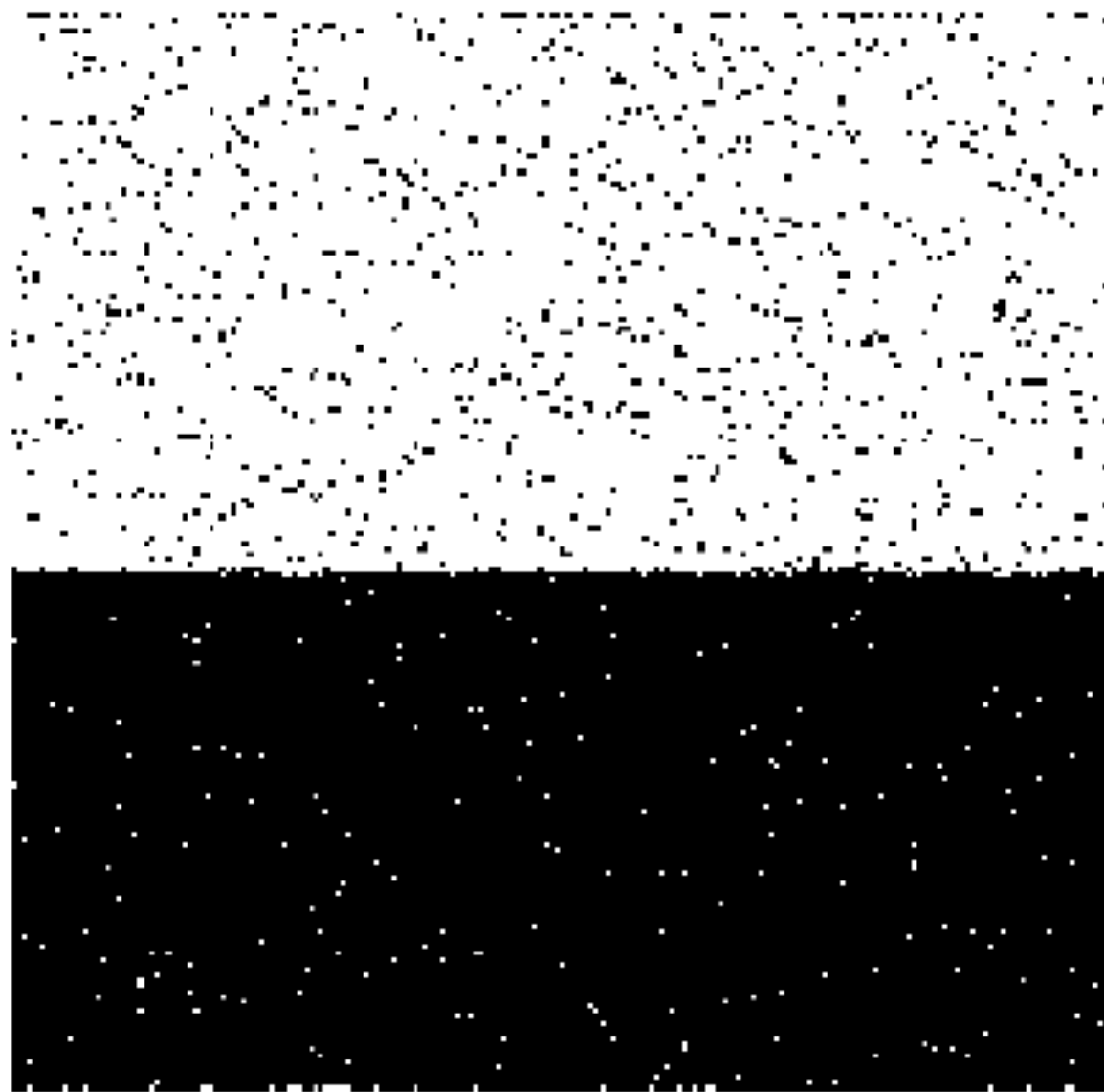
Drive

Phase coexistence: between two phases in a *single system* or between *two single-phase systems*
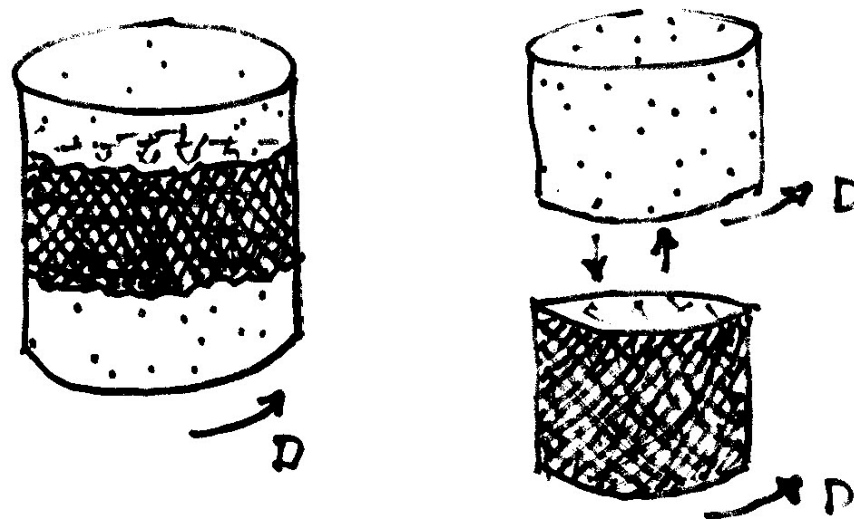
Equilibrium

Coexisting densities are *the same* in either case

ρ_V

ρ_L

Equilibrium: a phase is a phase is a phase

NESS

We *expect* the coexisting densities to be the same, but *are they*?

D

D

D

Phase coexistence in KLS model

Study phase separation in a **single system** under maximum drive, to identify coexisting densities at a given temperature T_R, well below T_c

For the same temperature, determine the coexisting densities for a **pair of uniform systems** under weak exchange

If notions of phase and phase coexistence are applicable to the NESS, the coexisting densities must be the same in the two cases
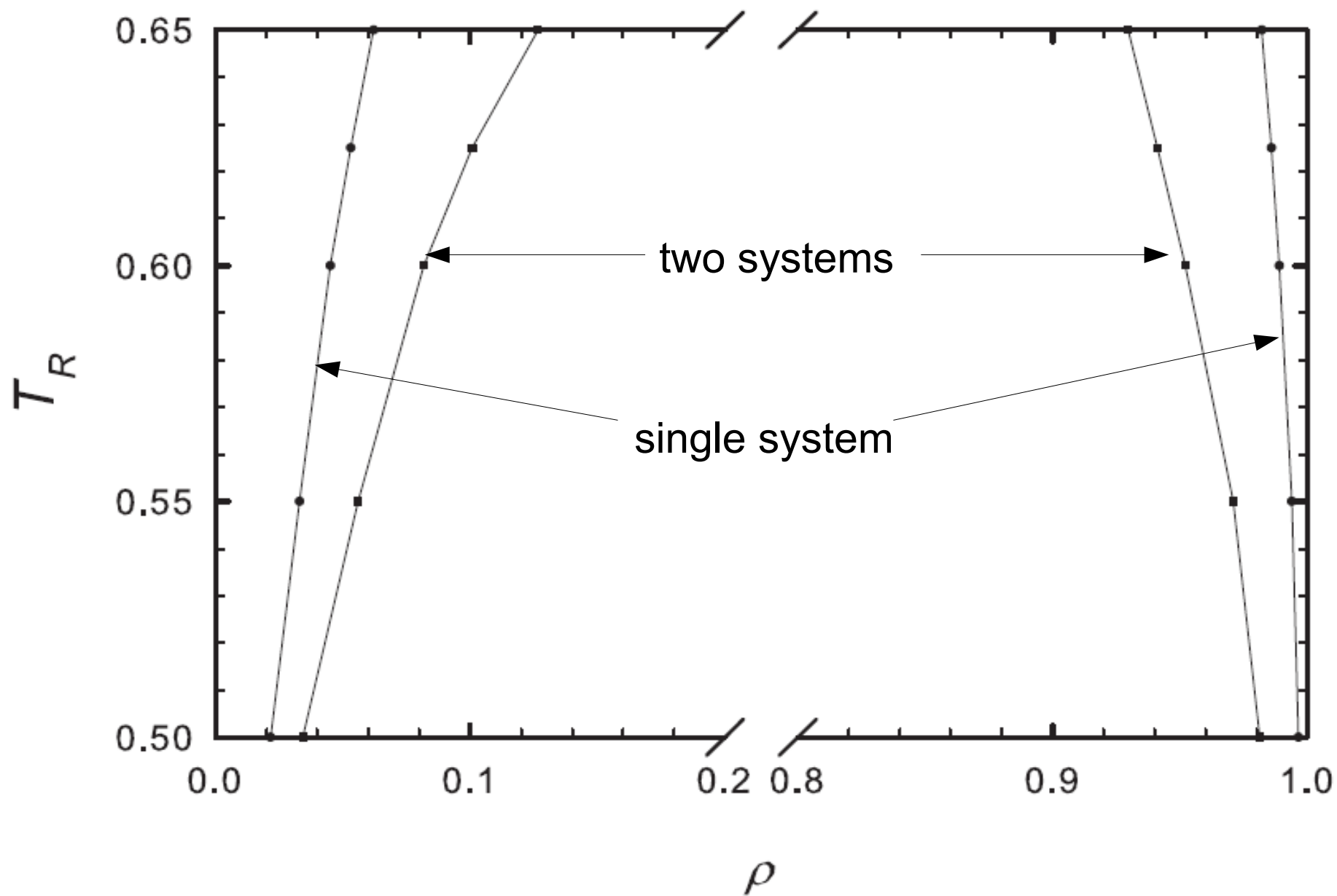
Results for T_R=0.5:

In phase-separated single system, coexisting densities are
 0.0224(4)   and   0.9965(1)

In uniform systems under weak exchange, coexisting densities are
 0.03595(3)   and   0.9826(1) - clearly incompatible w/prev result

- similar findings at other temperatures

Coexisting densities in single system and in coexisiting uniform systems: KLS model, maximum drive

Is the lack of well defined coexisting phases due to the drive/current in the KLS model?

To answer this I study another model, a ***two-temperature lattice gas***:

Sites on different sublattices (A/B) are in contact with different heat reservoirs (T_A/T_B)

There is no drive, no particle current, no anisotropy

The coexisting densies again depend on how the phases make contact

For T_A=0.4 and T_B = 0.55, the coexisting densities are:

0.9644(3) and 0.03001(3) (single system)

0.9542(6) and 0.0383(6)   (two systems, weak global exchange)

TABLE II: TTLG: coexisting densities in a single phase-separated system $(\rho_{L,1}, \rho_{V,1})$, and in a pair of uniform systems under weak global exchange $(\rho_{L,2}, \rho_{V,2})$.

T_A	T_B	$\rho_{L,1}$	$\rho_{V,1}$	$\rho_{L,2}$	$\rho_{V,2}$
0.30	0.50	0.9828(2)	0.0098(3)	0.9709(1)	0.01202(1)
0.35	0.55	0.9706(1)	0.02053(2)	0.951(3)	0.0240(16)
0.40	0.55	0.9644(3)	0.03001(3)	0.9511(15)	0.0333(4)

Conclusions (II)

Coexistence between systems in nonequilibrium steady states is not well defined: it depends on the manner in which the systems make contact.

The properties of coexisting phases depend on how they exchange particles between one another.

The notion of "phase" as a system with well defined intensive properties seems not to apply in NESS

Since this inconsistency is found in two of the simplest possible cases, independent of drive or anisotropy, there is good reason to believe it occurs in general

It appears unlikely that any formulation of steady-state thermodynamics can predict the properties of nonuniform systems or phase coexistence

III. In the spatially uniform case, the chemical potential is well defined and predictive: Can we define an entropy function?

The thermodynamic entropy has the property

$$\mu = -T \left(\frac{\partial S}{\partial N} \right)$$

understood as a finite difference for small systems. Thus we can evaluate S via integration.

Recalling the relation

$$\mu^* \equiv \frac{\mu}{k_B T} = \ln \frac{\rho}{\rho_{op}}$$

we have

$$S(N,L) - S(N\text{-}1,L) = \ln \frac{\overline{N}_{op}(L, N-1)}{N}$$

On a lattice of L^d sites. This defines the thermodynamic entropy.

## *Is the thermodynamic entropy for a NESS the Shannon entropy?*

$$S_S = -k_B \Sigma_i \, p_i \, \ln p_i$$

To evaluate S_S we need the stationary probability distribution, p_i

In collaboration with my student **Leonardo Ferreira Calazans**, we determine p_i for the driven NNE lattice gas on square lattices of LxL sites.

The results show that $S_{thermo} \neq S_S$

Potencial Químico - L = 6

Difference between thermodynamic and Shannon entropies at low drives

Violation of equality between Shannon and thermodynamic entropies:

$$\sum_{\mathcal{C}\in\Gamma(L,N)} P(\mathcal{C})\ln P(\mathcal{C}) - \sum_{\mathcal{C}\in\Gamma(L,N-1)} P(\mathcal{C})\ln P(\mathcal{C}) = \ln\frac{\overline{N}_{op}(L, N-1)}{N}$$

Violação (V) da relação 11 - L = 6

Violation of equality between Shannon and thermodynamic entropies:

$$\sum_{\mathcal{C}\in\Gamma(L,N)} P(\mathcal{C})\ln P(\mathcal{C}) - \sum_{\mathcal{C}\in\Gamma(L,N-1)} P(\mathcal{C})\ln P(\mathcal{C}) = \ln\frac{\overline{N}_{op}(L, N-1)}{N}$$

Violação (V) da relação 11 - L = 6

NNE model: difference between thermodynamic and Shannon entropies
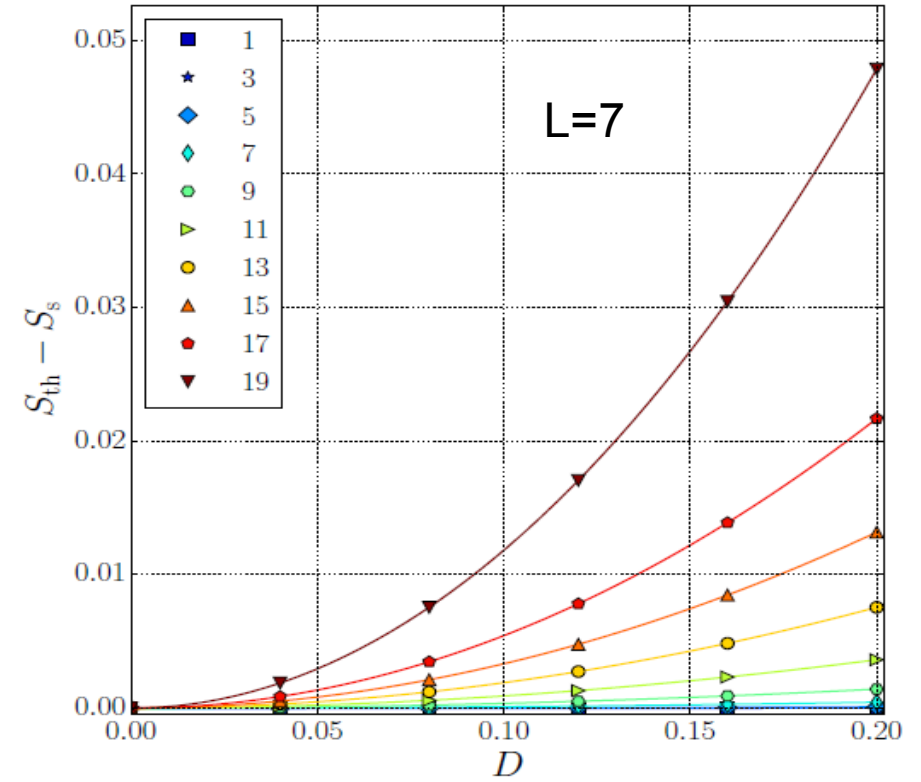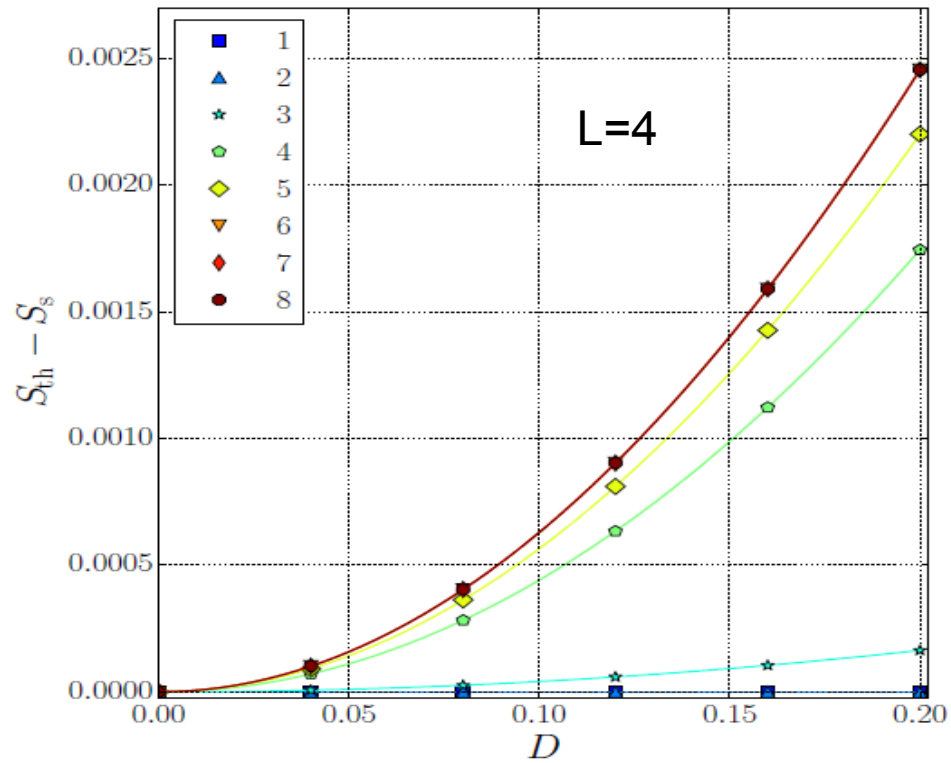
No difference for D=0; difference grows with L and N; proportional to D^2 for small D

Given the stationary probability distribution *Pest(C)*, we evaluate the mean energy transfer between the KLS system and reservoir R, as a function of the reservoir temperture T_R:

$$J_E = \frac{w_0}{2} \sum_{\mathcal{C},\mathcal{C}'} [E(\mathcal{C}') - E(\mathcal{C})][e^{E(\mathcal{C})/T} P_{est}(\mathcal{C}) - e^{E(\mathcal{C}')/T} P_{est}(\mathcal{C}')]$$

The value of *T* such that $J_E = 0$ defines the thermodynamic temperature of the KLS system. The thermodynamic entropy is found via:

$$S_{th}(E) = \int_{E_0}^{E} \frac{dE'}{T(E')} + S_0(E_0, N, V)$$

with $S_{th} = S_S$ in limit $T \to \infty$ (at infinite temperature, drive is irrelevant)
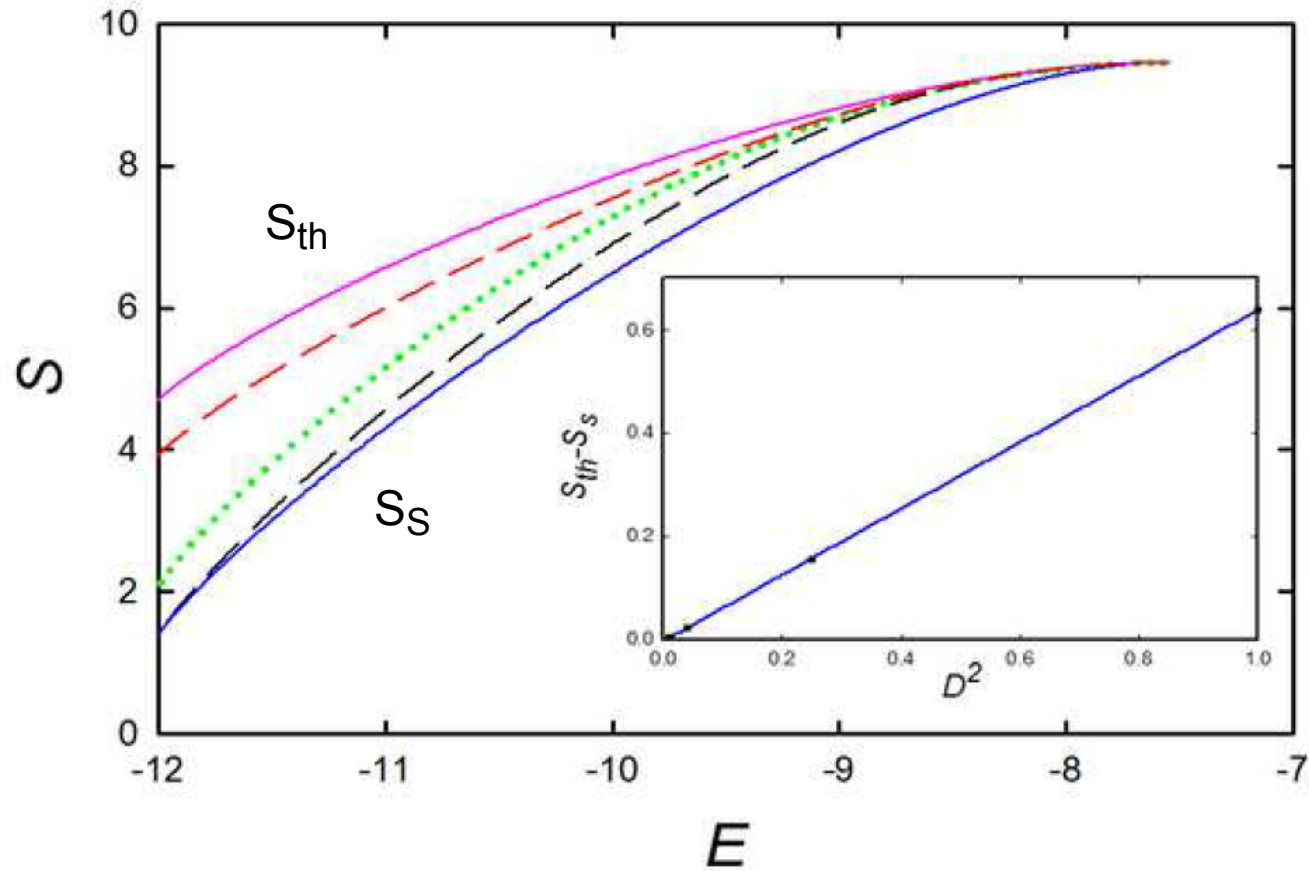
S_{th} and S_S in KLS model

FIG. 3: KLS lattice gas: thermodynamic and Shannon entropies versus energy for a system of $N = 8$ particles on a square lattice of 16 sites. Continuous curves: S_{th} (upper) and S_S (lower) for drive $D = 10$. Broken curves: S_{th} (upper) and S_S (lower) for drive $D = 1$. Dotted line: equilibrium entropy. Inset: $S_{th} - S_S$ versus D^2 for $E = -10$. The line is a linear fit to the data.
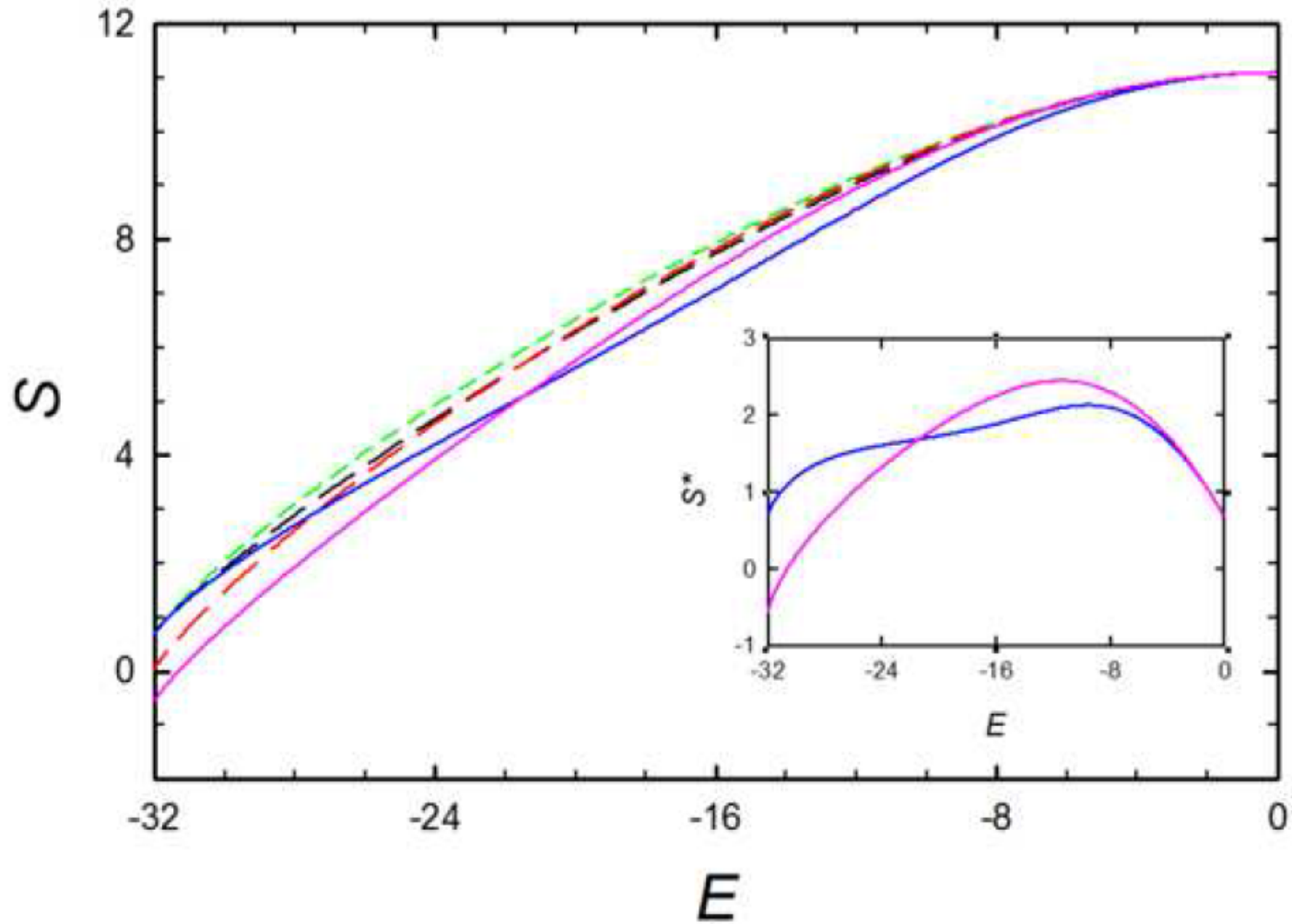
FIG. 4: Two-temperature Ising model on a square lattice of 16 sites. Dashed curves: S_{th} (lower at left) and S_S for $T_B = 2T_A$. Continuous curves: S_{th} (lower at left) and S_S for $T_B = 5T_A$. Short dashed curve: equilibrium entropy. Inset: entropies less the overall linear trend, $S^* \equiv S - 0.3251(E + 32)$ for $T_B = 5T_A$; S_{th}^* is the lower curve at left.

Who cares if $S_{thermo} \neq S_S$?

1. The two are always equal in equilibrium

2. The Shannon entropy is widely used as the entropy out of equilibrium (e.g., in stochastic thermodynamics)

3. The Shannon entropy is needed to connect thermodynamics with information

4. The Shannon entropy is the only extensive functional of the probability distribution

   Since the thermodynamic entropy of a NESS *is* extensive (we verify that the chemical potential is intensive),
   this implies that S_{thermo} cannot be written as a functional of p_i

Thank you!