

# **Inconsistencies in Steady State Thermodynamics**

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# OUTLINE

**Nonequilibrium steady states (NESS)**

**Steady state thermodynamics (Oono-Paniconi, Sasa-Tasaki, Pradhan et al)**

**Coexistence of NESS: definition of intensive variables  
effective temperature and chemical potential**

**Weak exchange, virtual contact and virtual reservoirs**

**Consistency and utility of intensive variables: zeroth law**

**Driven NNE lattice gas: consistent definition of chemical  
potential**

**Driven lattice gas with attractive interactions (KLS model):**

- need for effective temperature**
- violation of zeroth law**

# Coexistence of NESS

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

If A and B, at the same temperature, can exchange particles, and the net particle flux between them is zero, we say they coexist wrt particle exchange; we expect them to have the same value of “chemical potential”

Analogous definition for coexistence wrt energy exchange, temperature

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

We study lattice gases with stochastic dynamics

## Criteria for a valid chemical potential:

With  $\mu$  defined operationally as above, we stipulate two essential properties it must satisfy, to be a valid chemical potential:

1) (Zeroth law) If pairs of systems (A,B) and (A,C) separately satisfy the zero-flux condition, then, if B and C are allowed to exchange particles, the net flux should also be zero.

2) If systems A and B, at the same temperature, and initially isolated, with  $\mu_A \neq \mu_B$ , are brought into contact so that they may exchange particles, then the ensuing flux should reduce  $|\mu_A - \mu_B|$ , and should continue until the difference is null. In other words, knowing the functions  $\mu_A(\rho)$  and  $\mu_B(\rho)$ , of two systems in isolation should allow us to predict the direction of particle transfer when they are placed in contact, and the coexisting densities.

## Virtual exchange

Out of equilibrium, the stationary properties of the systems in contact in general depend on the *rate* of exchange of particles and/or energy.

To define the situation precisely, we consider the limit of vanishing exchange rates.

This is formalized in *virtual exchange*: determining the fluxes that would ensue *if exchange were permitted*, without actually transferring anything.

Particle exchange with a virtual reservoir with chemical potential  $\mu$

Choose a site at random, if vacant, insert particle w.p.

$$p_I = \min[1, e^{\beta[\mu - (E_{new} - E_{cur})]}].$$

If occupied, remove particle w.p.

$$p_R = \min[1, e^{\beta[-\mu - (E_{new} - E_{cur})]}]$$

Mean particle flux per exchange attempt:

$$\langle \Delta n \rangle_P = \sum_{\mathcal{C}} P(\mathcal{C}) \langle \Delta n \rangle_{\mathcal{C}}.$$

$P(\mathcal{C})$  is the probability distribution on configuration space

The flux is **zero** when the reservoir chemical potential equals that of the system

# Application to driven NNE lattice gas

In the NNE lattice gas a particle excludes nearest-neighbor sites – a hard-core repulsive potential

The model is athermal – no characteristic energy

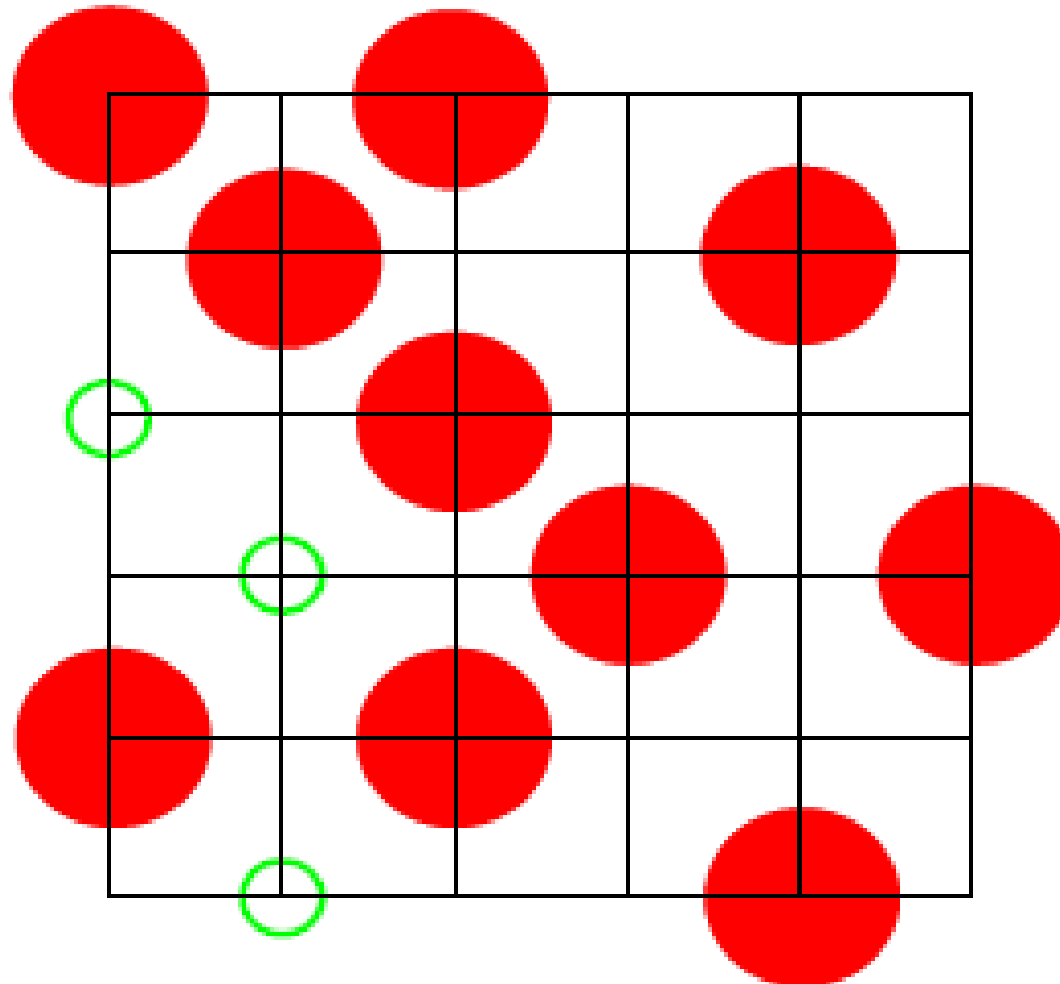
Only  $\mu^* = \beta\mu$  is of interest

Equilibrium dynamics: symmetric hopping attempts

Nonequilibrium (driven) dynamics: there is a preferred hopping direction

We study the model in the disordered phase

# NNE Lattice Gas



Red: occupied; green: open



Let  $\rho$  denote the particle density and  $\rho_{op}$  the density of *open* sites, i.e., of vacant sites with all their nearest neighbors also vacant. Since particles can only be inserted at open sites, we have, under virtual exchange between the NNE lattice gas and a particle reservoir,

$$\langle \Delta n \rangle_P = \rho_{op} \min\{1, e^{\mu^*}\} - \rho \min\{1, e^{-\mu^*}\} \quad (8)$$

so that the zero-current condition implies  $\mu^* = \ln(\rho/\rho_{op})$ . The chemical potential defined via Eq. (8) satisfies the zeroth law, regardless of whether the system is driven. To see this,

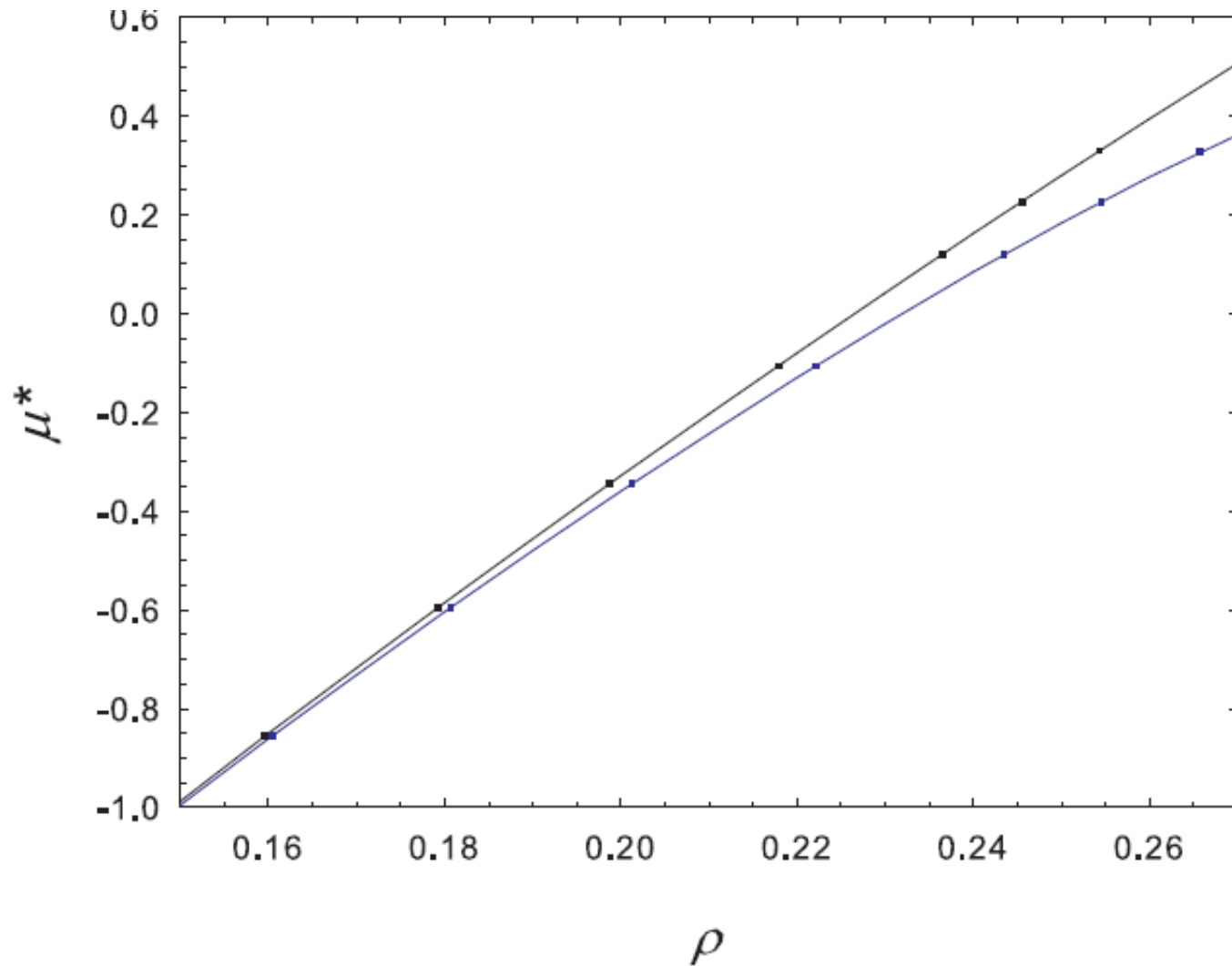


FIG. 1: NNE lattice gas: simulation results for  $\mu^*$  in equilibrium (black curve) and under maximum drive (blue curve), system size  $L = 80$ . Pairs of points sharing the same value of  $\mu^*$  represent coexisting densities in the equilibrium and driven systems under weak exchange. Uncertainties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

Given that  $\mu^*$  is an increasing function of density, for any value of the drive, Eq. (9) shows that if NNE models with different values of  $\mu^*$  are permitted to exchange particles, the ensuing flux will tend to equalize the chemical potential. In summary, we verify that  $\mu^*$  defined via the zero-current condition with a virtual reservoir satisfies the minimal conditions for a chemical potential, both in equilibrium and in a nonequilibrium steady state.

# DRIVEN LATTICE GAS WITH ATTRACTIVE INTERACTIONS: A FIRST ATTEMPT

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. The acceptance probability for a particle displacement  $\Delta\mathbf{x}$  is

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

Energy of configuration  $C$ :

$$E(C) = - \sum_{\langle i,j \rangle} \sigma_i \sigma_j$$

We attempt to describe coexistence between KLS systems using the approach employed for the NNE lattice gas.

Given a system  $S$  with density  $\rho_S$ , temperature  $T$  and drive  $D > 0$ , we determine  $\mu_S$  via the zero-current condition.

We then examine the possibility of coexistence between  $S$  and a nondriven (equilibrium) system  $S_0$  at temperature  $T$ , whose density is such that its chemical potential  $\mu_0$  equal to  $\mu_S$

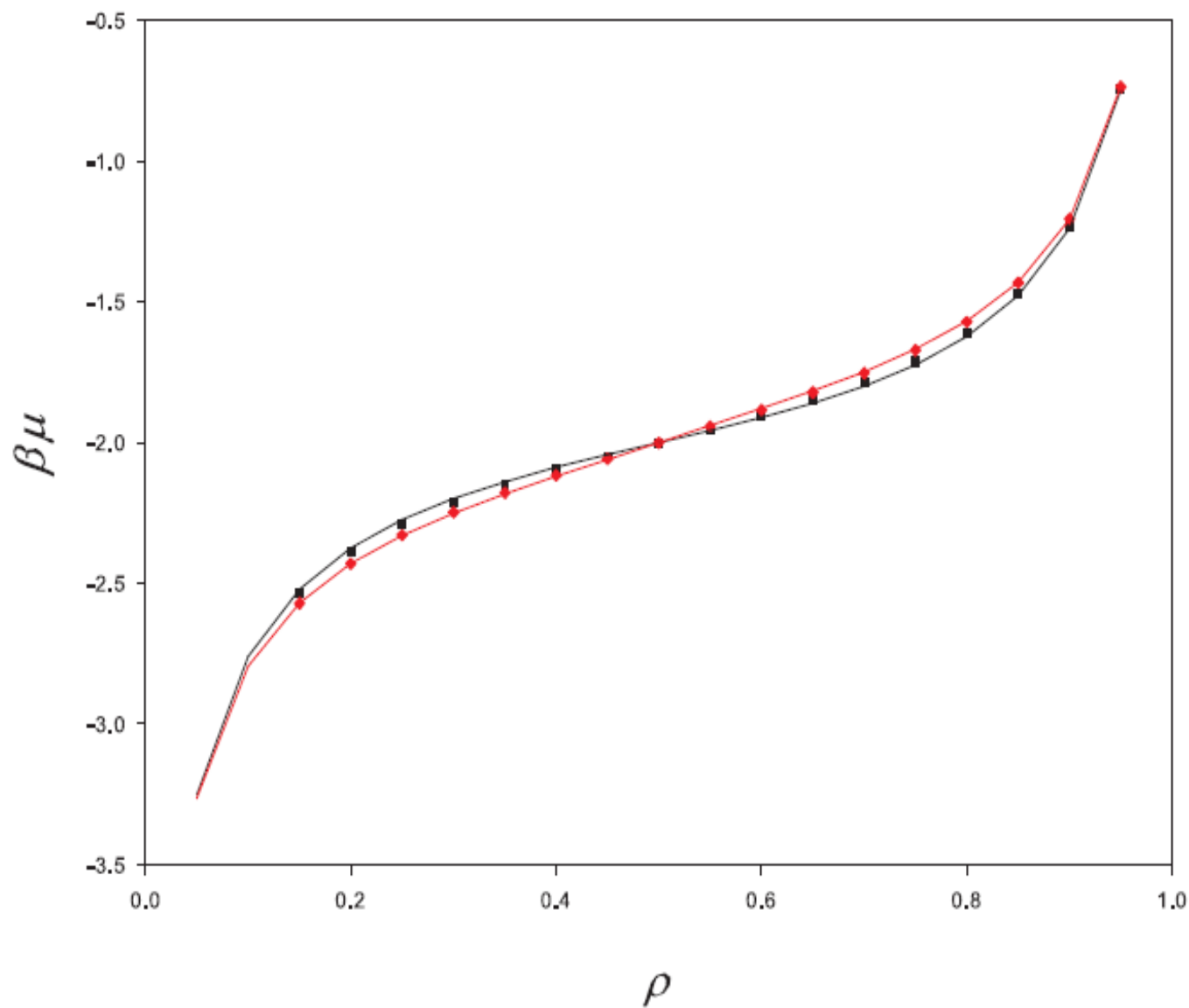


FIG. 3: KLS lattice gas: simulation results (points,  $L = 40$ ), and PA predictions (curves) for  $\mu^*$  in equilibrium (black) and under a strong drive,  $D = 10$ , (red), for temperature  $T = 1$ .

The results shown in Fig. 3 lead one to expect that if the two systems are initialized with the same density,  $\rho > 1/2$ , then particles will migrate from the driven to the undriven system, until the corresponding  $\mu$  values are equal

In fact, particles flow in the *opposite* sense!

Equating the effective chemical potentials of a driven and an undriven KLS system, does not predict the stationary densities when these systems are allowed to exchange particles.

The reason for this becomes apparent when we examine the energy transfer from the undriven to the driven system: on average, particle exchanges transfer energy from the driven to the undriven system

The nonzero energy flux implies that the two systems are not, in fact, at coexistence

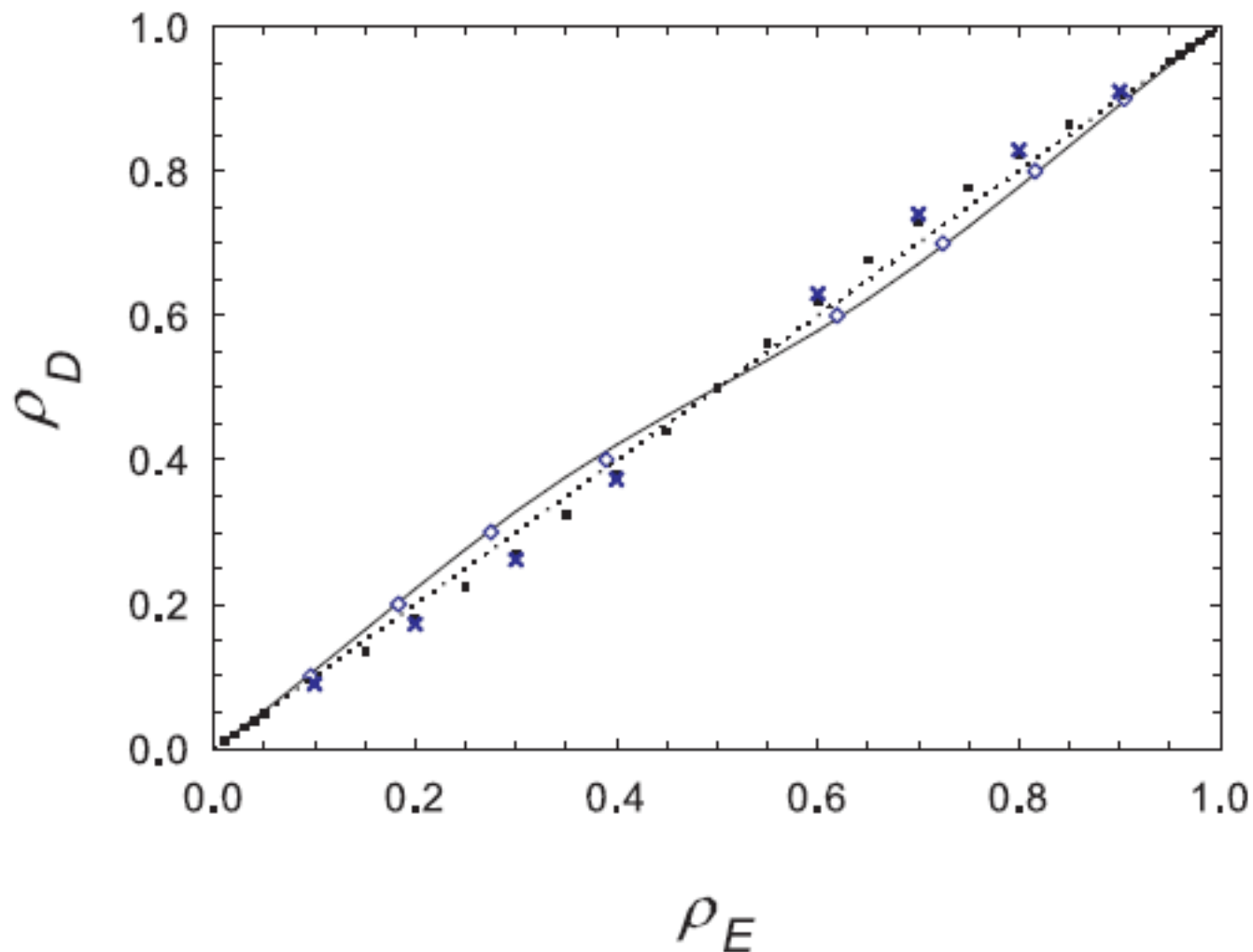


FIG. 5: KLS lattice gas: PA predictions for coexisting densities  $\rho_E$  (for  $D=0$ ) and  $\rho_D$  (for  $D=10$ ). Smooth curve: values obtained using equality of  $\mu^*$ ; black squares: stationary values obtained applying the PA to the two-lattice system under weak exchange,  $p_r = 10^{-3}$ ; blue diamonds: values obtained using equality of  $\mu^*$  as obtained via simulation; blue crosses: values obtained in simulations under weak exchange. The dotted diagonal line corresponds to  $\rho_D = \rho_E$ .



On average, the drive increases the energy of the system, since it tends to increase the likelihood of transitions with  $\Delta E > 0$  more than those with  $\Delta E < 0$ .

Under steady conditions, the energy increase due to the drive is balanced by the energy transfer to the reservoir: this is the so-called *housekeeping heat* associated with the stationary operation of a driven system.

Thus the reservoir temperature is *merely a parameter* in the definition of the transition probabilities; we shall refer to it as the “nominal temperature”  $T_n$

The effective temperature,  $T_e$ , of the driven system, if one can be defined, should be greater than  $T_n$ .

Define  $T_e$  via zero energy flux under virtual exchange

The effective temperature and chemical potential of  $S$  are determined by the conditions:

$$\langle \Delta n \rangle_S = \sum_{j=0}^q [\rho_S^+(-j) \min\{1, e^{\beta_e(\mu+j)}\} - \rho_S^-(j) \min\{1, e^{-\beta_e(\mu+j)}\}] = 0$$

$$\langle \Delta E \rangle_S = - \sum_{j=0}^q j [\rho_S^+(-j) \min\{1, e^{\beta_e(\mu+j)}\} - \rho_S^-(j) \min\{1, e^{-\beta_e(\mu+j)}\}] = 0$$

$\rho_S^+(-j)$ : density of vacant sites with  $j$  occupied neighbors

$\rho_S^-(j)$ : density of occupied sites with  $j$  occupied neighbors

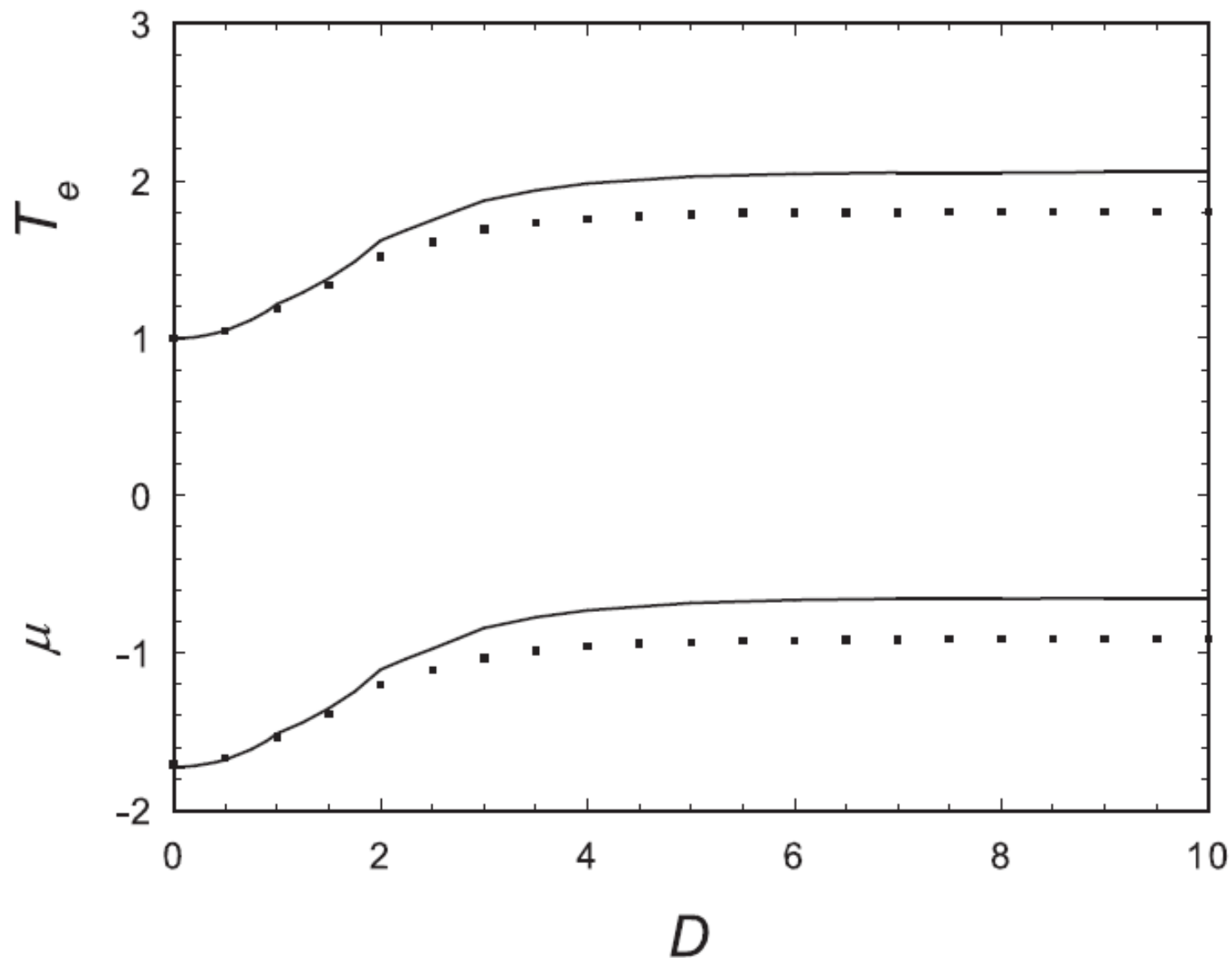


FIG. 6: KLS lattice gas: effective temperature  $T_e$  and chemical potential  $\mu$ , as defined via the zero-current conditions, as functions of drive  $D$  in a system at nominal temperature  $T_n = 1$  and density  $\rho = 0.75$ . Lines: PA; points: simulation.

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

Since  $S_0$  and  $R$  are in equilibrium, we have the detailed-balance relations,

$$\rho_0^+(-j) = e^{-\beta_e(\mu+j)} \rho_0^-(j)$$

We now ask whether  $S$  and  $S_0$  coexist, that is, whether the particle and energy fluxes between these systems are zero under virtual exchange.

Using detailed balance, the fluxes (from the nondriven to the driven system) are given by

$$\begin{aligned}
\langle \Delta n \rangle_{SS_0} &= \sum_{j_0} \left\{ \sum_{j < j_0} [\rho_S^+(-j) \rho_0^-(j_0) e^{\beta_e(j-j_0)} - \rho_S^-(j) \rho_0^+(-j_0)] \right. \\
&\quad \left. + \sum_{j \geq j_0} [\rho_S^+(-j) \rho_0^-(j_0) - \rho_S^-(j) \rho_0^+(-j_0) e^{\beta_e(j_0-j)}] \right\} \\
&= \sum_{j_0} \rho_0^-(j_0) \left\{ \sum_{j < j_0} e^{-\beta_e(j_0-j)} [\rho_S^+(-j) - e^{-\beta_e(\mu+j)} \rho_S^-(j)] \right. \\
&\quad \left. + \sum_{j \geq j_0} [\rho_S^+(-j) - e^{-\beta_e(\mu+j)} \rho_S^-(j)] \right\} \\
&= \sum_{j_0} \alpha(j) [\rho_S^+(-j) - e^{-\beta_e(\mu+j)} \rho_S^-(j)]
\end{aligned}$$

and

$$\langle \Delta E \rangle_{SS_0} = \sum_{j_0} j \alpha(j) [\rho_S^+(-j) - e^{-\beta_e(\mu+j)} \rho_S^-(j)],$$

where

$$\alpha(j) = \sum_{k=0}^j \rho_0^-(k) + \sum_{k=j+1}^q e^{\beta_e(j-k)} \rho_0^-(k)$$

Now  $\alpha(j)$  is an increasing function of  $j$  and has a ***different value*** for each  $j$

Thus the conditions  $\langle \Delta n \rangle_{SS_0} = 0$  and  $\langle \Delta E \rangle_{SS_0} = 0$  are in general ***distinct*** from those that define  $\mu$  and  $Te$   
In general the four conditions ***cannot be satisfied simultaneously***

For example, for  $\mu > 0$ ,  $\langle \Delta n \rangle_S = 0$  implies

$$\sum_{j_0} [\rho_S^+(-j) - e^{-\beta_e(\mu+j)} \rho_S^-(j)] = 0,$$

which is clearly different from the condition  $\langle \Delta n \rangle_{SS_0} = 0$ .

***We have therefore demonstrated a violation of the zeroth law: although  $S$  and  $S_0$  both coexist with  $R$ , in general they do not coexist with each other.***

Numerically, the violations appear to be quite small in the KLS model above the critical temperature

$T_n$	$\rho$	$D$	$T_e$	$\mu$	$\rho_0$	$\langle \Delta n \rangle_{\mathcal{S}\mathcal{S}_0}$	$\langle \Delta E \rangle_{\mathcal{S}\mathcal{S}_0}$	$\bar{\rho}_0$	$\bar{\rho}_{\mathcal{S}}$	$\bar{\mu}_0$	$\bar{\mu}_{\mathcal{S}}$
1	0.75	10	2.055866	-0.652531	0.749993	$3.3 \times 10^{-6}$	$3.5 \times 10^{-5}$	0.749990	0.750003	-0.652663	-0.652507
1	0.75	3	1.874951	-0.842986	0.749993	$2.0 \times 10^{-6}$	$2.9 \times 10^{-5}$	0.749990	0.750002	-0.842986	-0.842973
0.8	0.9	10	1.653732	0.128255	0.8999995	$-2.8 \times 10^{-6}$	$4.4 \times 10^{-5}$	0.900002	0.899998	0.128287	0.128224
1	0.4	10	2.133764	-2.499341	0.400019	$1.5 \times 10^{-6}$	$8.1 \times 10^{-6}$	0.400017	0.400002	-2.499350	-2.499333

TABLE I: PA results for coexistence of driven and undriven KLS lattices gases. The first three columns give the parameters of the driven system  $\mathcal{S}$ ;  $T_e$  and  $\mu$  are the effective parameters of  $\mathcal{S}$  obtained using a virtual reservoir.  $\rho_0$  is the density of the undriven lattice gas  $\mathcal{S}_0$  with temperature  $T_e$  and chemical potential  $\mu$ .  $\langle \Delta n \rangle_{\mathcal{S}\mathcal{S}_0}$  and  $\langle \Delta E \rangle_{\mathcal{S}\mathcal{S}_0}$  are the particle and energy fluxes between  $\mathcal{S}$  and  $\mathcal{S}_0$  under virtual contact. The final four columns give the stationary density and chemical potential (effective, in the case of  $\mathcal{S}$ ), under weak exchange.

Simulations show violations of the same order of magnitude

## **SUMMARY**

We have examined, in concrete, operational terms, the possibility of devising a steady state thermodynamics for driven lattice gases

In the case of the lattice gas with nearest-neighbor exclusion, our definition of an effective chemical potential turns out to be fully consistent, obeying the zeroth law, and capable of predicting the coexistence densities of systems with distinct values of the drive

We expect that this will be true of other models with purely excluded-volume interactions



Direct application of this approach to the KLS lattice gas clearly fails, motivating us to define an effective temperature  $T_e$

We then explore the possibility of predicting coexistence using equality of the effective temperature *and* chemical potential

A theoretical argument shows that the zeroth law is violated

We are left without a consistent SST applicable to systems capable of exchanging particles *and* energy

It appears that steady state thermodynamics is not viable for such systems