Thermodynamics and phase coexistence in nonequilibrium steady states

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Abstract. I review recent work focussing on whether thermodynamics can be extended to nonequilibrium steady states (NESS), in particular, the possibility of consistent definitions of temperature T and chemical potential μ for NESS. The testing-grounds are simple lattice models with stochastic dynamics. Each model includes a drive that maintains the system far from equilibrium, provoking particle and/or energy flows; for zero drive the system relaxes to equilibrium. Analysis and numerical simulation show that for spatially uniform NESS, consistent definitions of T and μ are possible via coexistence with an appropriate reservoir, if (and in general only if) a particular kind of rate (that proposed by Sasa and Tasaki) is used for exchanges of particles and energy between systems. The program fails, however, for nonuniform systems. The functions T and μ describing isolated phases cannot be used to predict the properties of coexisting phases in a single, phase-separated system.

1. Introduction

In recent decades the possibility of extending thermodynamics to far-from-equilibrium steady states has attracted considerable attention. By "thermodynamics" one understands a macroscopic description employing a small number of variables [1], although the set of variables needed to describe a nonequilibrium system may be somewhat larger than required for equilibrium. Thus in near-equilibrium thermodynamics, fluxes of mass, energy, and other conserved quantities enter the description [2,3]. This approach functions well in the hydrodynamic or local-equilibrium regime; here, by contrast, we are concerned with systems maintained far from equilibrium, in which the stationary probability distribution is very different from the Boltzmann distribution. Oono and Paniconi argued for the possibility of a steady-state thermodynamics (SST) on general grounds [4]. Sasa and Tasaki [5], extending their ideas, proposed definitions of the chemical potential and pressure in SST, and developed a theoretical analysis of the driven lattice gas; a numerical implementation in driven systems is discussed in [6]. More recently, Pradhan et al. [7] tested, via numerical simulation of driven lattice gases in contact, the consistency of the scheme proposed in [5], focussing on the validity of the zeroth law. They found that the zeroth law holds to good approximation, and suggested that observed deviations are due to nonuniformities induced by the contact itself. Of course, thermodynamics should hold *exactly* (not merely to good approximation), so it is essential to understand if the deviations are the result of approximations or are intrinsic to the theory.

While equilibrium thermodynamics has attained a state of maturity permitting an axiomatic formulation in terms of an all-inclusive entropy function [1], SST is far from such a stage. Rather than proposing formal schemes, I prefer to examine whether key intensive variables, such as chemical potential and temperature, can be defined operationally via *coexistence*. I proceed through a series of increasingly complex examples, beginning with spatially uniform systems before turning to nonuniform situations. I adopt, as minimal criteria for judging the validity of SST, that it be consistent, in the sense of the Zeroth Law, and that it have predictive value. For example, knowledge of the temperature and/or chemical potential of uniform systems as a function of the control parameters should permit one to predict the macroscopic properties of nonuniform systems.

I study two-dimensional stochastic lattice gases which are well established in equilibrium as simple models of fluids, and which, when perturbed from equilibrium, have a plausible interpretation as a fluid subject to an external drive or nonuniform temperature. Most of the conclusions are based on dynamic Monte Carlo simulations. Since the studies reported here are done far from any critical points, finite-size effects are minimal, as confirmed by comparing results for systems of linear size L ranging from 100 to 400 or 800. In the following section I discuss background and basic definitions. Section 3 is devoted to spatially uniform NESS, while in section 4 I turn my attention to nonuniform systems. Section 5 contains a brief summary and conclusions.

2. Intensive parameters, coexistence and reservoirs

Following the ideas of [4-6], I adopt *coexistence* as the basis for defining intensive parameters. Consider two systems, A and B, in steady states, that are permitted to exchange particles and/or energy. If the net flow of these quantities is zero, we say that A and B coexist with respect to (wrt) such exchanges, and assert that they share the same value of the associated intensive parameter. (If both A and B are each at equilibrium, "coexistence" implies *equilibrium* wrt exchange of the quantity of interest.) Thus if A and B coexist wrt both energy and particle exchanges, $T_A = T_B$ and $\mu_A = \mu_B$. (Here I consider single-component systems; the generalization to multicomponent systems is direct. In principle one can also define pressure in an analogous manner, but this is not required in the present discussion.) The Zeroth Law of thermodynamics states that if A and B coexist (wrt a certain type of exchange), and B and C coexist, then A and C must also coexist.

Now if one system, say B, is a *reservoir* of known temperature and/or chemical potential, we can use it to measure the corresponding properties of system A. The reservoir R is defined as having the following characteristics:

> Its intensive properties are invariant under exchange of particles and/or energy;

> Its mode of interaction with another system depends only on the intensive properties of the reservoir.

Suppose, for example, that R is a particle reservoir, characterized only by its dimensionless chemical potential $\mu^* = \mu/T$. (Here and in what follows I set Boltzmann's constant $k_B = 1$.) Let system A be an athermal lattice gas (i.e., in which the only interactions are of excluded volume) in which sites can be occupied by at most one particle. Then a suitable scheme of exchange between R and A is as follows. At rate w_R, each particle in A moves to the reservoir, and at rate w_I, each open site in A receives a particle from R. (An open site is one that may be occupied without violating the excluded-volume constraints.) A *could be* a simple lattice gas (no interactions beyond on-site exclusion), in equilibrium, in which case the mean fraction of occupied sites ρ follows $\dot{\rho} = -w_R\rho + w_I(1-\rho)$, while equilibrium statistical mechanics implies that $\rho_{eq} = z/(1+z)$ with $z = \exp[\mu^*]$. Equating $\dot{\rho}$ to zero at equilibrium, we have $w_I/w_R = \exp[\mu^*]$. Since w_R and w_I are properties of the reservoir not the system with which it makes contact,

this relation holds for exchange with *any* athermal lattice gas.

We use this simple observation to assert that, if A (an athermal lattice gas, in or out of equilibrium) is in contact with a particle reservoir R, and the net flux of particles between A and R is zero, then the dimensionless chemical potential of A is that of R: $\mu_A^* = \mu_R^*$. This definition of μ^* is equivalent to that proposed by Sasa and Tasaki [5]. For lattice gases with interactions beyond those of excluded volume (for example the case of nearest-neighbor attractive interactions discussed below), particle transfers in general imply energy transfers, and R should be a heat and particle reservoir [8].

3. Uniform driven systems

The considerations of the previous section lead directly to a definition of the chemical potential in athermal lattice gases. Let ρ_{op} be the fraction of *open* sites, that is, sites at which a particle may be inserted without violating the excluded-volume constraints. Exchange between a system A and a particle reservoir R leads to $\dot{\rho} = -w_R\rho + w_I\rho_{op}$, so that at coexistence,

$$\mu^* = \ln\frac{w_I}{w_R} = \ln\frac{\rho}{\rho_{op}} \qquad (1)$$

This is convenient computationally: in a simulation at fixed ρ, we simply monitor the fraction of open sites in the stationary state to estimate ρ_{op}; explicit exchange with a reservoir is not needed.

Now suppose that A and B are both athermal lattice gases, in spatially uniform steady states under their respective stochastic dynamics. Particle exchange between A and B may be implemented as follows: a fraction p_r of all transitions are exchange attempts, in which sites $\mathbf{x}$ and $\mathbf{y}$ are chosen at random in systems A and B, respectively. If $\mathbf{x}$ is occupied and $\mathbf{y}$ open, the particle at $\mathbf{x}$ is transferred to $\mathbf{y}$, and vice-versa. Now, in the limit $p_r \to 0$, each transfer is followed by an infinite sequence of transitions *within* systems A and B, allowing them to attain statistical independence. This permits us to write,

$$\dot{\rho}_A = -p_r[\rho_A\rho_{op,B} + \rho_B\rho_{op,A}]. \qquad (2)$$

Thus the zero-flux condition (coexistence) implies $\mu_A^* = \mu_B^*$, where the chemical potentials are those determined via contact with a reservoir. Moreover, if $\mu_A^* > \mu_B^*$, Eq. (2) implies a net flux of particles from A to B, and vice-versa, so that the final steady state under particle exchange is predicted by equating the (dimensionless) chemical potentials. (Here it is important to note that ρ_{op} is a nonincreasing function of density ρ, making μ^* an increasing function of density, as required by thermodynamic stability.)

The exchange scheme defined above is called *weak global exchange*: weak in the sense that $p_r \to 0$, global in the sense that exchange is allowed between any pair of sites. In the case of spatially uniform athermal systems under weak global exchange, the chemical potential, Eq. (1), satisfies the Zeroth Law and is predictive of the final state. In fact, the global exchange condition can be relaxed: even if $\mathbf{x}$ and $\mathbf{y}$ are *fixed sites* (representing the more realistic situation of local contact between two systems), the limit $p_r \to 0$ guarantees that the two systems can relax to spatially uniform distributions between exchange events [9].

I note briefly the generalization of the above scheme to continuous-space models. Let A be an athermal system and R a particle reservoir at chemical potential μ^*. Each particle in A has a rate ω to move to R, while R attempts to insert particles in A, at randomly chosen positions, at rate $\omega z V_A$, where V_A is the volume of A. Attempted insertions that satisfy all excluded-volume constraints are accepted. Denoting the acceptance probability for insertion as p_{ins}, we have for the mean number of particles in A, $d\langle N_A\rangle/dt = -\omega[\langle N_A\rangle - z p_{ins} V_A]$, or $\dot{\rho}_A \propto -\rho_A + z p_{ins}$, so that at coexistence, $\mu^* = \ln[\rho_A/p_{ins}]$. (Here ω is an arbitrary rate; weak exchange corresponds to the limit $\omega \to 0$.) In equilibrium, this formula corresponds to the Widom insertion method

[10]. For exchange between two athermal systems A and B, we assume transfer attempts from A to B at rate $\omega \rho_A$ and vice-versa. The zero-flux condition again corresponds to $\mu_A^* = \mu_B^*$.

The proposal outlined above for SST of uniform athermal systems has been tested on the lattice gas with nearest-neighbor exclusion (NNE) [8]. In this model the pair interaction is infinite if the distance between particles is ≤ 1, and is zero otherwise. The equilibrium NNE lattice gas has been studied as a discrete-space version of the hard-sphere fluid, and is known to exhibit a continuous (Isinglike) phase transition to sublattice ordering at a density of $\rho_c \simeq 0.36774$ [11].

Consider a NNE system on a lattice of L^d sites, with a fixed number of particles, and with a stochastic dynamics (e.g., particle hopping). Any particle displacement satisfying the NNE condition is accepted. If the transition rates obey detailed balance, the system relaxes to equilibrium.

The NNE lattice gas exhibits NESS under a drive that biases hopping [12], provided that boundaries along the drive direction are periodic. For single-particle nearest-neighbor hopping on the square lattice, we parameterize the drive such that hopping attempts in the $+x$ direction occur with probability $p/2$, and those in the opposite direction with probability $(1-p)/2$; the attempt probabilities for hopping in the $\pm y$ directions are $1/4$ as in equilibrium. Thus $p = 1/2$ corresponds to the unbiased (equilibrium) case, and $p = 1$ to maximum drive.

Simulating the NNE system on periodic lattices, I determine $\mu^*(\rho, p)$ for $p = 1/2$ (equilibrium) and $p = 1$ (maximum drive); the results are shown in Fig. 1. In the same figure, pairs of adjacent points represent the densities of driven and undriven systems under weak global exchange; the coexisting densities correspond, in fact, to equal values of μ^*, verifying the zeroth law, and showing that we can predict the densities of a driven system and nondriven system at coexistence by equating their respective chemical potentials.

An analogous scheme, for defining the chemical potential μ *and* temperature T of a nonathermal system in a NESS, is developed in [8]; the simplest example is the driven lattice gas with nearest-neighbor interactions, known as the Katz-Lebowiz-Spohn (KLS) model [13]. The interaction energy is $E = -\sum_{\langle i, j \rangle} \sigma_i \sigma_j$ where $\sigma_i = 0(1)$ denotes site i vacant (occupied), and the sum is over NN pairs of sites. (Each site may harbor at most one particle, but there is no prohibition of NN occupancy, as there is in the NNE model discussed above.) In equilibrium, this system is equivalent to the Ising model; on the square lattice the critical temperature is $T_c = 0.5673...$. The system evolves via particle-conserving NN hopping dynamics with a drive $\mathbf{D} = D\mathbf{i}$ favoring particle displacements along the $+x$ direction and inhibiting those in the opposite sense. (As before, we assume periodic boundaries along the drive.) The acceptance probability for a particle displacement $\Delta \mathbf{x}$ (to an unoccupied neighbor) is $p_a = f[(\Delta E - \mathbf{D} \cdot \Delta \mathbf{x})/T_\mathcal{R}]$, where the function $f(x)$ satisfies detailed balance, i.e., $f(-x) = e^x f(x)$, so that the system can achieve equilibrium if the drive $D = 0$. To begin we consider the widely used Metropolis acceptance probability,

$$p_a = \min\{1, \exp[-(\Delta E - \mathbf{D} \cdot \Delta \mathbf{x})/T_\mathcal{R}]\}. \tag{3}$$

Successful implementation of SST requires that we recognize two crucial points. First, on average, any nonzero drive performs work on the system (it facilitates transitions with $\Delta E > 0$ more than those with $\Delta E < 0$). To maintain a steady state, energy must flow to a heat reservoir $\mathcal{R}$, which is intrinsic to the KLS setup. In the above expressions for p_a, $T_\mathcal{R}$ is the temperature of this reservoir; since energy flows steadily from particle system to the reservoir, we might expect the temperature T_{KLS} of the particle system to be *greater than* $T_\mathcal{R}$.

Second, to measure the temperature and chemical potential, T_{KLS} and μ_{KLS}, we place the particle system in contact with a heat and particle reservoir R (distinct, of course, from $\mathcal{R}$), with parameters T and μ, and search for values that render the fluxes of particles *and* energy zero. Naively, one might suppose that exchanges of particles with reservoir R could be implemented using Metropolis rates, that is,
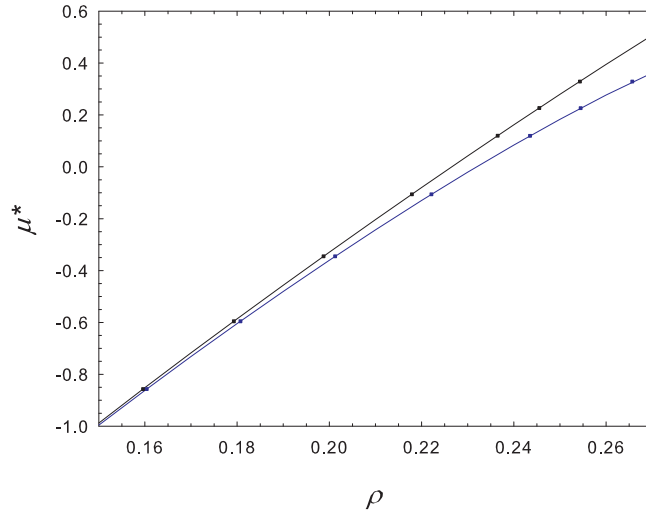
Figure 1. NNE lattice gas: simulation results for μ^* in equilibrium (black curve) and under maximum drive (blue curve), system size $L = 80$. Pairs of points sharing the same value of μ^* represent coexisting densities in the equilibrium and driven systems under weak exchange. Uncertainties are smaller than line thickness and symbol size.

$$w_{ins} = \omega \min\{1, e^{(\mu+j)/T_R}\} \tag{4}$$

and

$$w_{rem} = \omega \min\{1, e^{-(\mu+j)/T_R}\} \tag{5}$$

with j the number of occupied NNs of the target site, on insertion, and the number of occupied NNs of the particle to be removed, in the second case. As shown analytically in [8], *such rates lead to violations of the Zeroth Law.* The only exchange rates that yield consistent definitions of temperature and chemical potential are Sasa-Tasaki (ST) rates, which, in the present instance, follow,

$$w_{ins} = \omega \tag{6}$$

and

$$w_{rem} = \omega e^{-(\mu+j)/T_R} \tag{7}$$

The physical interpretation of ST rates is that, to be transferred, a particle must overcome an energy barrier; the energy of the state following the transfer has no influence on the rate of transfer.

Summarizing, for uniform systems it is possible, subject to certain restrictions, to define consistently intensive parameters such as temperature and chemical potential; equating these parameters enables one to predict the properties of coexisting systems in NESS.

4. Nonuniform systems

Given the encouraging results for uniform systems, I turn to nonuniform NESS. The macroscopic behavior of systems subject to a nonuniform drive, or in which nonuniformities arise due to phase separation, are important potential applications of SST.

To begin I consider the NNE lattice gas subject to a nonuniform drive [9]. I study a lattice of $L \times L$ sites (with L ranging from 200 to 800) divided into two parts by applying a drive in half of the system. The boundaries between the driven and undriven regions are parallel to the drive. Of particular interest are the stationary density and chemical potential profiles ($\rho(j)$ and $\mu^*(j)$, respectively), in the direction perpendicular to the drive. If SST functions correctly, the coexisting bulk densities ρ_0 and ρ_D should be given by the equal chemical potential condition (implying $\rho_D > \rho_0$), and the chemical potential profile should be flat, i.e., $\mu^*(j) = \mu^*(\rho_0, 0) = \mu^*(\rho_D, D)$.

Initially, particles are distributed uniformly over the lattice. For the densities and system sizes considered here, the system attains a stationary state well before 5×10^6 time units, the time allowed for relaxation; averages are calculated over a period of 5×10^6-10^7 time units, following relaxation.

As shown in Fig. 2, the stationary state of the half-driven system is very different from that predicted by SST. The density is higher in the *undriven* region, contrary to the prediction obtained equating the chemical potentials of driven and undriven systems. The chemical potential profile is clearly nonuniform, more so than if the particle density were uniform at the average global density. Particles have migrated so as to increase severalfold the difference in chemical potential between the two regions, rather than diminish it! Notice that this discrepancy exists regardless of how, or whether, we define the chemical potential: Densities which coexist in uniform systems do not coexist when the systems make contact along an edge. (One might suppose that reducing the rate of particle hopping across the boundary between driven and undriven regions might resolve the conflict, as this would correspond to weak exchange between the regions. Such a reduction in fact only serves to accentuate the discrepancy [9].)

Finally, I consider phase coexistence in lattice gases with attractive interactions. Here nonuniformities arise spontaneously, due to phase separation, rather than being imposed via a nonuniform drive. The KLS model provides a simple realization of phase separation far from equilibrium. At high temperatures, the state with uniform density is stable, but (in two or more dimensions) below a certain critical value of T_R, the system segregates into high- and low-density phases separated by a narrow interface. In simulations, the coexisting densities ρ_L and ρ_V are determined by analyzing the density profiles in the direction perpendicular to the drive [14]. In these studies ST rates are used for hopping in this direction, since this, as noted above, is necessary for consistent definitions of T and μ. In a second set of studies, uniform systems are prepared at densities ρ_L and ρ_V, and allowed to attain coexistence under weak global exchange. As shown in Fig. 3, the coexisting densities in the pair of uniform systems are quite different from those observed in the single phase separated system. Studies of phase separation in another nonequilibrium lattice gas (with different sublattices in contact with reservoirs at distinct temperatures) yield similar results [14]. We are thus led to the conclusion that phase coexistence between NESS is not well defined: the coexisting densities depend not only on the drive and the reservoir temperature(s), but on the details of how the two phases make contact and exchange particles.

5. Conclusions

Summarizing, we have seen that steady-state thermodynamics appears viable for spatially uniform nonequilibrium steady states. It appears to fail, however, in the presence of nonuniformities, due either to a nonuniform drive, or to phase separation. This is an area in which simulation can help to answer fundamental questions regarding the scope
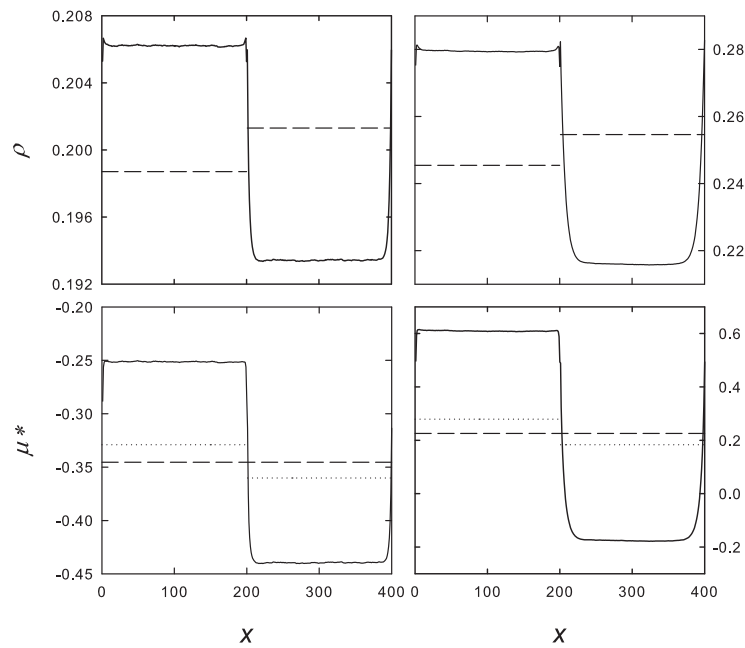
Figure 2. Density (upper) and chemical potential (lower) profiles in the half-driven NNE model. Drive $D = 0$ for $x \leq 200$; $D = 1$ for $x > 200$. Global densities $\overline{\rho} = 0.2$ (left) and 0.25 (right). In the upper panels the dashed lines show the coexisting densities predicted by equating chemical potentials. In the lower panels the dashed lines show the expected uniform value of the chemical potential, and the dotted lines show the chemical potentials for the isolated systems, each at density $\overline{\rho}$.
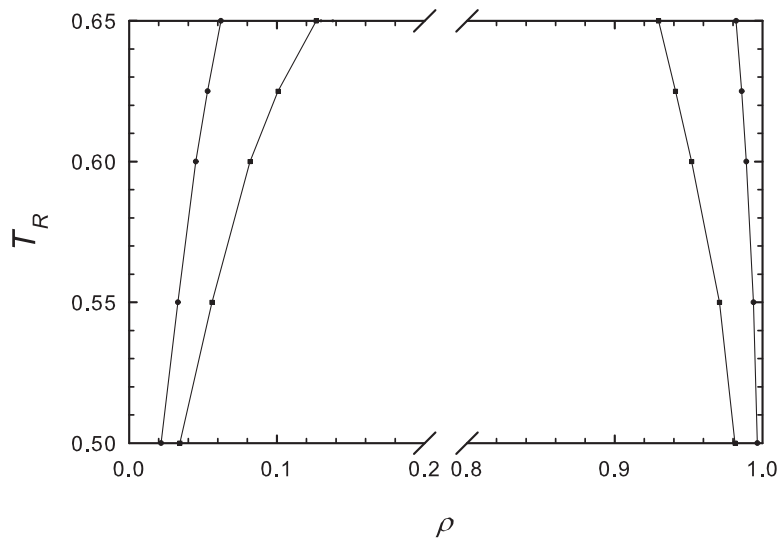

Figure 3. KLS model: coexisting densities ρ_L (right) and ρ_V (left) versus reservoir temperature T_R. The points nearer the vertical axes correspond to the single phase-separated system; those further from the axes correspond to uniform systems under weak global exchange. System size $L = 400$. Error bars smaller than symbols.

of thermodynamics. Further studies, of off-lattice systems, and of systems of particles with momentum, are needed to assess the validity of SST under more realistic conditions. Nevertheless, given the inconsistencies found in the simple models discussed here, it appears unlikely that a consistent thermodynamics of far-from-equilibrium systems is possible.

Acknowledgments

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