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Novel Phase Transitions in Biased Diffusion of Two Species.

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Abstract. – We investigate biased diffusion in a stochastic lattice gas with equal numbers of oppositely «charged» particles, interacting only through an excluded-volume constraint. Particle-particle exchanges are allowed, but occur on a much slower time scale than the dominant particle-hole exchanges. With increasing particle density, the system orders first into a charge-segregated state, and disorders again near complete filling, through first-order transitions which turn second order at higher densities. A set of mean-field equations reflects the variations of the density profiles in the different phases.

Driven stochastic lattice gases are amongst the simplest model systems in which the statistical mechanics of non-equilibrium steady states can be studied [1]. Suggested roughly a decade ago [2], the «standard model» consists of particles hopping stochastically to neighboring empty sites, subject to the usual Ising energetics and a driving field which favors (suppresses) jumps along (against) a particular lattice direction. It rapidly attracted considerable attention, revealing such unexpected behavior as generic singularities in thermodynamic functions at all temperatures [3] and non-Hamiltonian fixed points controlling the critical behavior [4].

Following the spirit that led from the Ising model to spin-1 [5] or Potts [6] models, it is natural to consider generalizations of the «standard model», to more than one species of particles. Surprisingly, even the simplest generalization, to two species of particles which i) are biased to move in opposite directions and ii) do not interact apart from obeying a strict excluded-volume constraint, possesses a rich phase diagram [7]. Controlled by particle density and drive, the system exhibits a line of first-order phase transitions, from a disordered, high-current phase to a «locked« phase with nearly vanishing current. Moreover, depending on the aspect ratio of the system, ordered phases with different topologies are found to coexist [8]. Mean-field theory [9, 10] confirms these findings and also predicts a crossover from first- to second-order transitions at low bias and high density [9], which has not yet been observed in simulations.

Interpreting the particles as cars, moving in differing directions, such two-species systems can serve as traffic models [11]. Fast ionic conductors, which motivated the «standard model», include materials with two mobile ion species [12]. For both of these applications, it is paramount that the excluded-volume constraint is strictly enforced, so that a particle may not exchange its position, or, equivalently, its charge, with a neighbor. On the other hand, in another application [13], the two species of particles model water droplets with opposite electric charges in a microemulsion. Here, charge transfer from one droplet to another occurs rapidly, mimicking the interchange of particles in the model. Thus motivated, we consider here a modification of the original two-species model [7] to a system in which both particle-hole and particle-particle exchanges are allowed. A convenient way to incorporate both the opposite bias and the distinct identity of the two species is to endow the particles with opposite «charges» and to impose an external «electric» field. However, we emphasize that our particles do *not* interact with the usual long-range Coulomb interactions. Thus, particle exchanges are now effectively «charge» exchanges, while particle-hole exchanges model diffusion. In general, these processes occur on different time scales. We denote by γ the ratio of the *rates* associated with charge-exchange and diffusion.

In one spatial dimension, the steady state of this model on a ring is exactly known [14]. In systems with open boundary conditions, one observes the unusual phenomenon of spontaneous symmetry breaking in a one-dimensional system with effectively short-ranged interactions [15].

In this letter, we focus on two-dimensional, fully periodic systems, and extend the density-field phase diagram of [7] to include a third axis: γ. Employing both simulations and coarse-grained equations of motion, we investigate the shape and nature of the resulting *surface* of order-disorder transitions: For small, fixed γ, the system first orders, via a first-order transition reminiscent of the $\gamma = 0$ case, and then disorders again, via a continuous transition, as the mass density is increased. The remainder of this letter is devoted to a brief description of our methods and results, leaving details to be published elsewhere [16]. We conclude with some open questions.

We consider a fully periodic square lattice with $L_x \times L_y$ sites, each of which may be empty or occupied by a single particle. The particles carry either positive or negative charge, and are driven by a uniform external electric field E, directed along the $+y$-axis. Thus, we require two occupation variables, $n_+(i)$ and $n_-(i)$, being equal to 0 or 1, depending on whether a positive or negative charge is present at site i. There are no other interparticle interactions. We study different mass densities $\overline{m} \equiv \sum_i \{n_+ + n_-\}/L_x L_y$, but restrict ourselves to zero total charge $\sum_i \{n_+ - n_-\}$. In the absence of the drive, the dynamics does not distinguish particles of differing charge: both types hop randomly to neighboring empty sites, with a rate Γ, independent of direction. In addition, a pair of nearest-neighbor particles may exchange their charges, with rate $\gamma\Gamma$. The electric field introduces a bias into these two processes, breaking the charge symmetry. In one Monte Carlo step (MCS), $L_x L_y$ nearest-neighbor pairs are chosen at random. If a particle-hole pair is encountered, an exchange takes place with rate $\Gamma \equiv 1$, unless the particle attempts to move against the field (*i.e.* $\Delta y = \mp 1$ for a $\pm$ charge), in which case the probability of exchange is lowered to $\exp[-E]$. Similarly, if a pair of distinct particles is chosen, exchange occurs with probability γ and $\gamma \exp[-E]$, the latter governing moves against the bias.

These rates, and the associated Master equation for the time evolution of $P[\{n_q\}, t]$, *i.e.* the probability of finding our system in the configuration $\{n_q\}$ at time t, fully specify our dynamics at the microscopic level. Starting from an arbitrary initial configuration, we expect

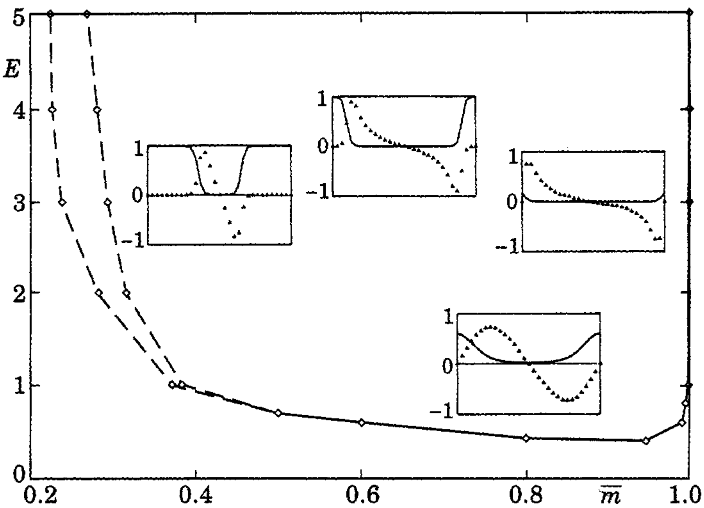

Fig. 1. – Phase diagram, for a 30×30 system at $\gamma = 0.01$. The solid line marks continuous transitions, while the two dashed lines denote the upper and lower spinodal lines (based on runs of $2 \cdot 10^5$ MCS) associated with the first-order transitions. The insets show four profiles of the hole (solid line) and charge (triangles) densities along the y-axis. Their parameters correspond to their approximate locations in the phase diagram: $(E, \overline{m}) = (3.0, 0.31)$; $(3.0, 0.8)$; $(3.0, 0.99)$; and $(0.5, 0.8)$.

the system to settle into an inherently non-equilibrium, t-independent steady state, $P^*[\{n_q\}]$. Our focus is the behavior of P^* as a function of $\overline{m}$, E, γ, L_x and L_y. First, note that the steady state is known exactly, namely $P^* \propto 1$, on the two planes $E = 0$ and $\overline{m} \equiv 1$, $\gamma > 0$. In the former case, particles diffuse randomly, so that the homogeneity of P^* follows rather trivially. In the latter regime, there are no holes, so that only charge exchanges take place. Relabelling negative charges as «holes» and positive charges as «particles», the dynamics reduces to the biased diffusion of a single species of particles, which is also associated with a uniform P^* [17]. Thus, in both regimes configurations are disordered, with homogeneous charge densities. Further, we expect that disorder also prevails once γ exceeds a critical γ_c. In particular, at $\gamma = 1$, the dynamics of a positive (negative) charge no longer distinguishes a negative (positive) particle from a hole. We, therefore, argue that spatial inhomogeneities are impossible for either charge density. Thus, we focus on rather small γ, in order to observe the onset of spatial structures. We finally note that the line $\overline{m} \equiv 1$, $\gamma = 0$ is singular in that the system remains completely frozen in its initial configuration.

Next, we turn to the results from Monte Carlo simulations. Different square systems, with $L \equiv L_x = L_y$ ranging from 20 up to 40, and two values of γ, 0.01 and 0.1, were investigated, with most of the data taken at $L = 30$ and $\gamma = 0.01$. After discarding the first $2.5 \cdot 10^4$ MCS, measurements were taken every 250 MCS, each run lasting at least $2 \cdot 10^5$ MCS. Our results are summarized in an E-$\overline{m}$ phase diagram, shown in fig. 1. For small E, typical steady-state configurations are disordered. As E increases, we identify a threshold, $E_c(\overline{m}, \gamma)$, beyond which both charge and hole density develop spatial inhomogeneities: particles gather to form a single strip, transverse to the field, while the rest of the lattice remains essentially empty. To distinguish the flat profiles of disordered configurations from the charge-segregated, ordered ones, we measure the order parameter [7] $Q \equiv \sum_y \left\{ \sum_x [n_+(i) - n_-(i)]/L \right\}^2 / L\overline{m}$, where x and y are the coordinates of site i, noting that the quantity in the curly brackets is just the charge density profile of a given configuration as a function of y. Further, we measure the charge current J. To analyze the nature of the transitions, we compute the averages $\langle\cdot\rangle$ of Q, J, and of their fluctuations.

Crossing the transition line $E_c(\overline{m}, \gamma)$ with $\overline{m}$ fixed below a critical $\overline{m}_0(\gamma)$, both $\langle Q\rangle$ and $\langle J\rangle$ change abruptly and exhibit hysteresis. The time trace of long runs (10^6 MCS) close to the transition shows switching between the ordered and disordered states, so that the associated order parameter histogram exhibits two well-separated peaks, indicating a first-order transition similar to the $\gamma = 0$ case. As $\overline{m}$ increases, the hysteresis loops exhibited by $\langle Q\rangle$ and $\langle J\rangle$ shrink, becoming unobservable for $\overline{m} \geqslant \overline{m}_0(\gamma)$. Here, histograms of Q show a single peak, moving smoothly away from the origin as the transition line is crossed. While weak first-order transitions cannot be completely ruled out, these characteristics, supported by a preliminary study of the fluctuations of Q, are certainly consistent with second-order transitions for $\overline{m}_0(\gamma)$. Clearly, more detailed finite-size analyses are needed before a final conclusion can be reached.

We now turn to characteristic profiles. While charge density profiles, measured just beyond the first-order transition, are similar to those found in [7] (left inset of fig. 1), those at higher densities differ substantially, exhibiting three, rather than two, regimes (top inset in fig. 1): Reminiscent of a sandwich, the small (large) y part of the strip consists mainly of $+(-)$ charges, while the middle section shows both species mixing, by virtue of charge exchange. Particles and holes are separated by sharp interfaces, contrasting starkly with the diffuse interface between positive and negative charges. The small residual current, in this «locked» state, is almost entirely due to charge exchange. In contrast, just above the second-order line, the charge profile is essentially harmonic (bottom inset in fig. 1). Here, the hole profile never vanishes (typically, one hole per row), so that the system orders, but does not lock up fully.

As shown in fig. 1, disorder prevails for densities near zero and one, separated by a region of ordered phase. For $\gamma = 0.01$ and $L = 30$, the disordered region near complete filling is confined to the line $\overline{m} \equiv 1$ and a small sector at the bottom right of fig. 1. In fact, for $E \geqslant 3.0$, the removal of a *single* particle from a completely filled lattice suffices to order the system! In contrast, preliminary data for $\gamma = 0.1$ indicate that the system is disordered at *any* E, if $\overline{m} > 0.98$. The holes act as catalysts for the charge segregation process, creating a domain of predominantly positive charge separated by a sharp interface from a similar, negatively dominated region below. Expelled from either region, the holes remain localized at the interface. Due to periodicity, a second interface must be present which, in contrast, remains diffuse, being dominated by charge exchange. An example of this regime is displayed in the inset on the right (fig. 1), the result of removing five pairs of particles.

While the microscopic dynamics specified above is easily simulated, it is not susceptible to a theoretical analysis. To proceed, we attempt a «coarse-grained» description, postulating equations of motion for the slow variables in the system. Here, these are the densities for the two species, $\varrho_\pm(r, t)$, as functions of continuous space and time. An easy, if somewhat naive, route is to start from the microscopic evolution equations for the average local occupation numbers, truncate all correlations, and take the continuum limit. Introducing the operator $\overleftrightarrow{\nabla}$, defined via $u\overleftrightarrow{\nabla}v \equiv u\vec{\nabla}v - v\vec{\nabla}u$, the resulting equations are [16]

$$(1/\Gamma)\,\partial_t\varrho_\pm = \vec{\nabla}\cdot\{\phi\overleftrightarrow{\nabla}\varrho_\pm \mp \hat{y}\Delta\phi\varrho_\pm\} + \gamma\vec{\nabla}\cdot\{\varrho_\mp\overleftrightarrow{\nabla}\varrho_\pm \mp \hat{y}\Delta\varrho_\mp\varrho_\pm\}. \tag{1}$$

Here, $\phi \equiv 1 - (\varrho_+ + \varrho_-)$ is the local hole density. Γ sets the (overall) time scale, and $\Delta\hat{y}$ denotes the coarse-grained bias. The equations manifest the equivalent structure of particle-hole and charge exchanges, the ratio of the associated rates being γ. The symmetry under the combined operation $\varrho_{\pm} \to \varrho_{\mp}$ and $\Delta \to -\Delta$ is self-evident. Imposing periodic boundary conditions on the square $x, y \in (0, L]$ and the constraints $\int \phi = L^2(1 - \overline{m})$ and $\int \varrho_+ = \int \varrho_-$, eqs. (1) form the basis of the theoretical analysis of our model.

The existence of homogeneous stationary solutions to (1) is trivial, due to the conservation laws. The presence of *inhomogeneous* solutions can be demonstrated following [7]: Searching for inhomogeneities in the y-direction only, we can integrate eqs. (1) once and eliminate the charge density $\varrho_+ - \varrho_-$ in favor of ϕ. Introducing $u \equiv \sqrt{1 + \gamma/\phi(1-\gamma)}$ leads to the potential form $u'' = -\partial_u V(u)$, with $V = (C/4\gamma)[u^2 - 4 \ln u - u^{-2}] - (1/8)[u^2 + (1-\gamma)^{-2} u^{-2}]$. Here, prime denotes $\mathrm{d}/\mathrm{d}(\Delta y)$, and $C\Delta$ is the charge current, playing the role of an integration constant. The existence of periodic solutions, which map into spatially inhomogeneous structures in our model, is now apparent. Charge and hole density profiles can be found by numerical integration, and closely resemble the ones from simulations, in the appropriate regions of parameter space. In particular, near complete filling the profiles clearly reflect the localization of the hole density at the sharp plus-minus interface.

From linear stability analysis, we find that the homogeneous solutions become unstable if the scaled bias [9, 10] $\varepsilon \equiv \Delta L_y$ exceeds a critical $\varepsilon_H(\gamma, \overline{m})$. The most relevant perturbation is associated with the smallest wave vector along $\hat{y}$, *i.e.* $(0, 2\pi/L_y)$, so that $\varepsilon_H = 2\pi\sqrt{[1-(1-\gamma)\overline{m}]/[(1-\overline{m})((2-\gamma)\overline{m}-1)]}$. Thus, this instability can only occur if $1/(2-\gamma) < \overline{m} < 1$. For $\gamma \geqslant 1$, the homogeneous phase is always stable. Fluctuations will undoubtedly affect this mean-field value of $\varepsilon_H(\gamma, \overline{m})$. However, since it mirrors the shape of the observed phase boundary rather closely, we may assume that it provides some insight into the γ-dependence of the latter. In particular, we expect the ordered phase to shift to higher values of m, as γ increases, vanishing entirely at some critical γ_c. Preliminary data for $\gamma = 0.1$ confirm this picture.

In summary, we have studied the stochastic, driven dynamics of a simple lattice gas of two oppositely charged species. Extending a previous study [7], charges may exchange with holes, but also with one another, on a much slower time scale. Homogeneous and inhomogeneous configurations are observed, separated by a surface of first- and second-order transitions in a phase diagram spanned by particle density, bias and ratio of time scales. On the analytic side, the two phases are reflected in the steady-state solutions of a set of coarse-grained equations of motion, with a linear stability analysis providing some insight into the onset of an instability.

The behavior of the system is determined by the competition of two processes: on the one hand, biased particle-hole exchanges lead to mutual blocking of opposite charges, stabilized by the excluded-volume constraint. On the other hand, such inhomogeneities are slowly eroded by charge exchanges, so that particles of, say, positive charge drift slowly, on a time scale controlled by $1/\Gamma\gamma$, through the block formed by the negative charges. Once free, they quickly traverse the depleted region, only to rejoin the positively dominated strip, on a time scale controlled by $1/\Gamma$. Thus, for sufficiently small γ the charge inhomogeneity can be maintained in steady state. However, the dependence on density and system size is clearly quite intricate: for instance, inhomogeneous configurations must destabilize when typical diffusion times of a particle through dense and depleted regions become comparable.

In addition to finite-size analyses, there are numerous other open questions. To address just a few of these, we are investigating the details of the ordering process as $\overline{m}$ is lowered from complete filling, characterizing it, *e.g.*, by a hole-hole correlation function. Further, we are exploring the nature of the order-disorder transition as a function of γ, at fixed E and $\overline{m}$. This will also yield information about the shape of the line $\overline{m}_0(\gamma)$, where the first-order transitions turn second order. While one might be tempted to label the latter a non-equilibrium tricritical line, a considerable amount of work is required to establish its nature with some confidence.

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