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Nonequilibrium field-induced phase separation in single-file diffusion

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Using an analytically tractable lattice model for reaction-diffusion processes of hard-core particles we demonstrate that under nonequilibrium conditions phase coexistence may arise even if the system is effectively one-dimensional as e.g. in the channel system of some zeolites or in artificial optical lattices. In our model involving two species of particles a steady-state particle current is maintained by a density gradient between the channel boundaries and by the influence of an external driving force. This leads to the development of a fluctuating but always microscopically sharp interface between two domains of different densities which are fixed by the boundary chemical potentials. The internal structure of the interface becomes very simple for strong driving force. We calculate the drift velocity and diffusion coefficient of the interface in terms of the microscopic model parameters.

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1 Introduction

Diffusion of particles in long and narrow channels has a long history of theoretical investigation and has recently become a focus also of experimental interest e.g. in the study of molecular diffusion in zeolites [1], diffusion of colloidal particles in confined geometry [2] or optical lattices [3] and granular diffusion [4]. In many such channel systems the particles cannot pass each other. This mutual blocking phenomenon is known as single-file effect and leads to subdiffusive behaviour [5, 6]. Among other things the single-file effect is responsible for low reaction effectivity in microporous catalysts [7] and is thus of technical importance in chemical engineering. The single-file effect occurs also in biological systems, examples being the motion of ribosomes along the m-RNA during protein synthesis [8, 9] or transport by molecular motors along microtubuli or actin filaments [10]. In single-file systems the longitudinal motion is the most important dynamical mode and makes such processes amenable to treatment by one-dimensional models [11, 12].

Low-dimensional diffusive particle systems are of great interest also from a thermodynamic point of view. In open boundary systems, *kept far from equilibrium* by maintaining a steady state particle current, various unexpected kinds of critical phenomena have been discovered in recent years, including boundary-induced phase transitions, phase separation and spontaneous symmetry breaking, see [11, 12] and references therein for a review. These finite-temperature critical phenomena have no counterpart in thermal equilibrium since in one-dimensional systems with short range interactions there is no mechanism that could prevent the creation and growth of an island of the minority phase inside a domain of the majority phase. Therefore it is not possible to have a phase-separated equilibrium state with a stable and microscopically sharp interface between two fluctuating domains characterized by different values of the order parameter.

Most of these nonequilibrium critical phenomena are not yet well-understood. Given the interesting diffusion properties as well as the potential for applications to catalytic reactions it would thus be interesting to explore critical phenomena in low-dimensional reaction-diffusion systems in more detail. Specifically, in this paper on one-dimensional reaction-diffusion systems we would like to investigate the existence and microscopic properties of interfaces between coexisting nonequilibrium domains which are macroscopically different.

In order to set the stage and sharpen the question we begin with some remarks of general nature and mention some results relevant to our approach. Systems of diffusing and reacting particles are usually described macroscopically by hydrodynamic equations for coarse-grained quantities like the particle density [13]. The density then represents the local order parameter specifying the spatial evolution of the macroscopic state of the system. Such equations are usually proposed on a phenomenological basis, paradigmatic examples being the Burgers equation for driven diffusive systems with particle conservation [14] or the Fisher equation for reactive systems without conservation law [15, 16]. These equations are in general non-linear and exhibit shocks in some cases. This means that the solution of the macroscopic equations may develop a discontinuity even if the initial particle density is smooth. This means that in these systems phase separation may occur. The shock represents the interface between the two thermodynamically distinct phases.

This hydrodynamic description of phase separation is, however, not fully satisfactory. It provides no insight into the microscopic origin of the phenomenon, and it gives no information about the internal structure of the shock. It could very well happen that in a particle system described on hydrodynamic (Eulerian) time scale by an equation which has shock solutions no corresponding microscopic discontinuity would be observable on less coarse-grained space or time scales which are experimentally relevant particularly for the quasi one-dimensional systems referred to above. In order to understand the structure of shocks and the emergence of such nonlinear behaviour from the microscopic laws that govern the stochastic motion and interaction of particles it is therefore necessary to *derive* the macroscopic equations from the microscopic dynamics rather than postulating them on phenomenological grounds.

Carrying out this programme starting from Newton's equation of motion constitutes a rather difficult problem. However, a substantial body of results of this nature has been obtained for specific one-dimensional stochastic lattice models [17, 18], the best-studied example being the asymmetric simple exclusion process (ASEP) [19, 20]. In this basic model for a driven diffusive system each site k on the infinite integer lattice $\mathbb{Z}$ is either empty ($n_k = 0$) or occupied by at most one particle ($n_k = 1$). A particle on site k hops randomly to the site $k + 1$ with rate D_r and to the site $k - 1$ with rate D_l, but only if the target site is empty. Otherwise the attempted move is rejected. The jumps occur independently in continuous time with an exponential waiting time distribution. For a single particle this is a biased random walk which on large scales describes Brownian motion driven by a constant external force. The exclusion rule mimics a short-ranged hard-core interaction potential between particles. In the hydrodynamic limit the system is described by the Burgers equation which exhibits shocks. Such a shock discontinuity may be viewed as the interface between stationary domains of different densities.

Moreover, there are a number of exact results about shocks in lattice gas models for driven diffusive systems [21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31], in reaction-diffusion systems [27, 31, 32, 33, 34, 35] (where shocks appear as Fisher waves on the macroscopic scale) and in spin-flip systems [27, 31, 35] where shocks correspond to domain walls [36]. It has emerged that in all these models the macroscopic shock discontinuity originates from a microscopically sharp increase of the local particle density, i.e., a decrease of the mean distance between particles that can be observed on the scale of a few lattice units (which typically represents the size of particles). The discontinuity itself performs a biased random motion with a constant mean speed and diffusive mean square displacement. The existence, structure, and dynamical properties of microscopically sharp shocks in lattice models for reaction-diffusion systems are the issues on which the present work focuses.

These results for the dynamical behaviour and microscopic properties of shocks have been obtained for infinite or periodic particle systems. In most physical applications, however, one has to study finite systems with open boundaries where particles are injected and extracted. This is crucial to take into account as – in the absence of equilibrium conditions – the boundary conditions determine the bulk behavior of driven systems, even to the extent that boundary induced phase transitions between bulk states of different densities occur [37, 38, 39]. Qualitatively, the strong effect of boundary conditions on the bulk can be attributed to the presence of steady-state currents which carry boundary effects into the bulk of the system. Quantitatively, exact results for the steady state of the ASEP have helped to show that part of the nonequilibrium phase diagram of driven diffusive systems with open boundaries, viz. phase transitions of first order, can be understood from the diffusive motion of shocks [40, 41], in analogy to the Zel'dovich theory of equilibrium kinetics of first-order transitions. In a series of recent papers [42, 43, 44, 45] these considerations, originally formulated for conservative dynamics, have been extended to non-conservative reaction-diffusion systems with open boundaries. As in equilibrium, the nonequilibrium theory of boundary-induced phase transitions requires the existence of shocks which are microscopically sharp. Therefore, the study of the microscopic structure of shocks in open systems is essential for understanding boundary-induced first order transitions and the phase separation phenomena associated with it.

After this survey we are finally in a position to precisely state the objective of this work. All the systems studied so far allow only for the presence of a single species of particles. No exact results have been reported so far for non-stationary travelling waves in open two-component systems, i.e. where two diffusive particles species A, B react with each other to form an inert reaction product or undergo a cracking or coagulation reaction ($B \rightleftharpoons 2A$). In order to address this question we adapt the strategy suggested in [27] to two-component systems: We take as initial distribution of particles a shock distribution with given microscopic properties and look for families of models