

On The Diffusion of Sticky Particles in 1-D

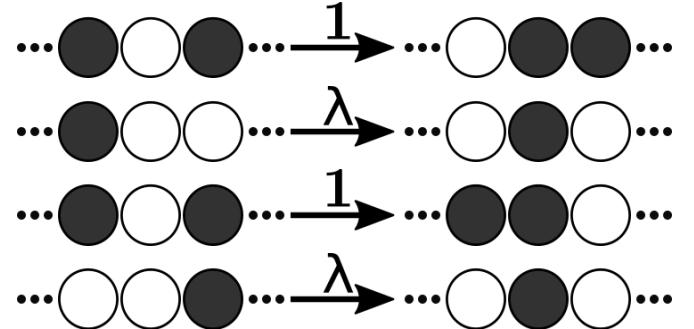
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The 1D Ising model is the simplest Hamiltonian-based model in statistical mechanics. The simplest interacting particle process, is the Symmetric Exclusion Process (SEP), a 1D lattice gas of particles that hop symmetrically and cannot overlap. Combining the two gives a model for sticky particle diffusion, SPM, which is described here. SPM dynamics are based on SEP with short-range interaction, allowing flow due to non-equilibrium boundaries conditions. We prove that SPM is also a detailed-balance respecting, particle-conserving, Monte Carlo description of the Ising model. Neither the Ising model nor SEP have a phase transition in 1D, but the SPM exhibits a non-equilibrium transition from a diffusing to a blocked state as stickiness increases. We present a fully non-linear, analytic, mean-field solution, which has a crossover from positive to negative diffusion constant. Simulations in the positive-diffusion region agree with the analytics. The negative diffusion constant in fact indicates a breakdown of the mean-field approximation, with close to zero flow and breaking into a two-phase mixture, thus the mean field theory successfully predicts its own demise. The simplicity of the model suggests a wide range of possible applications.

Lattice gases are a ubiquitous tool for modelling complex systems from biology to traffic[1–7]. Analytically solvable cases involve non-interacting or excluding particles [8, 9]. But in any real system of interest the moving objects interact. Many models tackle the situation where the diffusing object interact with the substrate, but despite the clear application-relevance there is surprisingly little work considering interactions between the moving particles. One reason for this is that the interactions introduce nonlinearities in analytical models, which makes them challenging to solve, at least outside of limits in which they can be linearised. This is unfortunate, because it is precisely these nonlinearities which introduce interesting behaviours - discontinuities at the oxide-metal interface, diffusion instability, to name just a few.

In this paper we will investigate a simple one-dimensional model, the “Sticky Particle Model” or SPM, specified in Figure 1, which contains such an interaction, and we will explore the impact this has, particularly on behaviour in the large-scale limit. One might contrast this approach (making a simple microscopic model and trying to learn about large-scale interface growth from it) with approaches such as the KPZ equation [10–12] (where one analyses the extreme large-scale dynamics using universality classes). The SPM, is based upon the symmetric exclusion process [13–18]; it differs from the original in that adjacent particles separate with rate $\lambda = 1 - \zeta$ instead of their normal hopping rate, 1. It is in fact a version of the KLS model [19, 20] in 1-dimension without an applied field, which is itself similar to the dynamics used to analyse the Ising model by Kawasaki [21]. It seems that this symmetric model has not been researched much, at least in terms of its dynamics, because the model with the applied field is so interesting; however, it seems that the simple symmetric model exhibits complex unexpected behaviour when a concentration gradient is applied. It is worth noting that the rates specified

FIG. 1. White circles indicate particles, dark circles indicate empty sites (vacancies). Particles randomly move into adjacent vacancies with rate 1 (having rescaled time for notational convenience), unless there is a particle behind the position they’re moving from, in which case they move with rate $\lambda = 1 - \zeta$.



in Figure 1 obey detailed balance, with an energy proportional to the number of particle-particle adjacencies in the system. It seems that space of highly-local exclusion models is so tightly constrained in one-dimension that there is no option but to comply with the detailed balance condition.

The model described in Figure 1 is very simple, but numerical simulation shows that it is capable of a wide range of behaviours, such as those shown in Figure 5. We will discuss these numerical results in more detail in Section , but first let us analyse the model behaviour using analytic means. Because the model contains interactions, the normal methods for the analytic solution of SEP don’t work; thus, we’ll just derive a mean field theory Let the spacing between lattice sites be a , τ_0 be the free-particle hopping timescale and the time-averaged (or ensemble-averaged, assuming ergodicity) occupation probability of the i^{th} lattice site be ρ_i . One may show

that, in the mean-field approximation regime,

$$\begin{aligned} \tau_0 \frac{\partial \rho_i}{\partial t} &= (1 - \rho_i) [(1 - \zeta \rho_{i-2}) \rho_{i-1} + (1 - \zeta \rho_{i+2}) \rho_{i+1}] \\ &\quad - \rho_i [2\zeta \rho_{i-1} \rho_{i+1} - (3 - \zeta) (\rho_{i-1} + \rho_{i+1}) + 2], \end{aligned}$$

Switching to the continuum limit by taking $a \rightarrow 0$, and neglecting $\mathcal{O}(a^4)$ terms, we may reexpress this as a conserved flow J as follows:

$$\begin{aligned} \frac{\partial \rho}{\partial t} &= -\frac{\partial J}{\partial x}, \\ J &= -\frac{a^2}{\tau_0} A(\rho) \frac{\partial \rho}{\partial x}, \\ A &= 1 - \zeta \rho(4 - 3\rho). \end{aligned}$$

Thus, the MFT says that the particles should diffuse with a diffusion coefficient $A(\rho)$ which depends upon the local density.

Continuum MFT Predictions

First let us consider some limits. As $\zeta \rightarrow 0$ (in other words, as the model becomes a simple exclusion model), $A \rightarrow 1$, which makes sense. Likewise, in the dilute limit $\rho \rightarrow 0$, $A \rightarrow 1$, reflecting the fact that it becomes a dilute lattice gas and therefore the interactions between particles become irrelevant as they never meet. Conversely, in the full limit $\rho \rightarrow 1$, $A \rightarrow 1 - \zeta$; this makes sense because we now have a dilute gas of vacancies, which hop with rate $\lambda = 1 - \zeta$. One may observe that the continuum limit MFT has a symmetry under $\rho \mapsto \frac{4}{3} - \rho$; thus, the dynamics should be symmetric under a density profile reflection around $\rho = \frac{2}{3}$. This is where A always attains its extremal value, $1 - \frac{4}{3}\zeta$, hence for $\zeta > 3/4$ the diffusion coefficient becomes negative in regions with $\frac{2}{3} - \frac{\sqrt{\zeta(4\zeta-3)}}{3\zeta} < \rho < \frac{2}{3} + \frac{\sqrt{\zeta(4\zeta-3)}}{3\zeta}$. Finally, it is possible to show that solutions to the continuum MFT containing domains with a negative diffusion coefficient are linearly unstable; thus, if we try to have a flow containing ρ for which $A(\rho) < 0$, the density of the medium should gravitate towards a density for which $A(\rho) \sim 0$, so instead of observing “backwards diffusion” we would see an extremely slow flow or no flow at all. The MFT implies that the transition to this critically slowly-flowing regime happens suddenly, like a phase transition; this is something we can check with our numerics.

Steady-State Flow Through a Block

It is possible to solve the continuum MFT in a steady state on a finite domain, say $x \in (0, L)$. The continuity

equation implies that $J(x) = J_0$, and by integrating both sides of that equation with respect to x we find that

$$J_0(x - x_0) = -\frac{a^2}{\tau_0} \rho [1 + \zeta \rho (\rho - 2)], \quad (1)$$

a cubic equation which can be solved to give $\rho(x)$. If we impose Dirichlet boundary conditions on this system, say $\rho(0) = \rho_0$ and $\rho(L) = \rho_L$, we find that

$$J = \frac{a^2}{L\tau_0} [\rho_0 - \rho_L + \zeta (\rho_0 [\rho_0^2 - 2] - \rho_L [\rho_L^2 - 2])]. \quad (2)$$

We may consider applying small concentration gradients across a block by setting $\rho_0 = \rho_M + \frac{1}{2}\delta\rho$ and $\rho_L = \rho_M - \frac{1}{2}\delta\rho$. Doing so, we find that the effective diffusion coefficient of the block $D = \frac{\partial J}{\partial \delta\rho}|_{\delta\rho=0}$ obeys

$$\left. \frac{\partial J}{\partial \delta\rho} \right|_{\delta\rho=0} = \frac{a^2}{L\tau_0} [1 - \zeta \rho_M (4 - 3\rho_M)], \quad (3)$$

a result we will make use of when we come to analyse our numerics in Section .

NUMERICAL RESULTS

We now have some MFT predictions about the SPM, and a few ideas about when those predictions might be invalid. Thus, it is prudent for us to test them out numerically. There are a few different methods which could have been used, but we chose to calculate using the excellent **KMCLib**[22] package, which implements the Kinetic Monte Carlo algorithm (essentially the same as the Gillespie algorithm[23]) on lattice systems. **KMCLib** has the advantage that it is python-wrapped C++, and thus quite easy to use whilst at the same time being quite computationally efficient; thus it was fairly easy for us to carry out large numbers of differently-parametrised serial **KMCLib** jobs on the **Eddie3** computing cluster here at Edinburgh. The codes used are kept here [24].

As we have MFT predictions about flow in a block, we can try to simulate that situation using KMC. In the bulk, the transition rates are simply those described in Figure 1. At the boundaries, referred to as the “top” and “bottom” of the block, there are 2 layers of lattice sites what switch between being full and empty with rates such that the time-averaged occupation can be specified to match the desired boundary conditions; there are then chances for particles to spawn and despawn with rates depending upon the occupation of these boundary layers. In the end, the intention is that these boundaries should reproduce the effect of having particle reservoirs attached to the ends, which is something we check in the output by inspecting the time-averaged occupations of sites near the boundary. We have used this setup to explore three scenarios, discussed in the following sections. In each

of these we refer to a boundary condition configuration by (ρ_0, ρ_L) , with ρ_0 and ρ_L being the bottom and top boundary densities respectively. When we measure flow rate in such a situation, we perform a specified number of Gillespie steps and count the number of particles entering at the top e_L , leaving at the top l_L , entering at the bottom e_0 , leaving at the bottom l_0 , as well as the Gillespie time interval T that elapses during those steps; we then have an estimate of the overall flow rate J via

$$J = \frac{e_0 - e_L + l_L - l_0}{2T}. \quad (4)$$

We can also count the total number of particles in the system in order to measure the average particle density, although we need to make sure that it is correctly time-averaged; this is done by updating a histogram of particle numbers as the simulation progresses. In each of our calculations, we make the initial configuration by randomly filling the system with particles and vacancies in such a way that the initial density should be $\frac{1}{2}(\rho_0 + \rho_L)$, and then run the system for a sufficient number of equilibration steps to destroy any initial transients.

Varying λ with Fixed Boundary Conditions

The MFT suggests that a transition, from a steady flow regime to a critically slow flow regime, might occur as λ varies. We test this by holding the boundary densities constant whilst changing λ , and measuring the particle density as well as the mean, variance and skewness of the flow rate. If such a transition does indeed occur, we should expect to see a divergence in one of these moments. We have done this with 4 sets of boundary conditions as shown in Figure 2. In each case we used systems of length 64 (length 32 gives similar results), running them for 400000 Gillespie steps for equilibration followed by 10000 measurement runs of 1000 steps interspersed with relaxation runs of 16000 steps. This way we could gather statistics about flow rates and densities in a well-equilibrated system. Specifically, we generate a pool of 10000 samples of flow rate and density, from which we can calculate estimates of the sample mean, variance, skewness and kurtosis of both quantities.

Firstly, we should note that we only really have an MFT prediction for the flow rate as a function of λ . Technically we could attempt to predict the density as well, but $\rho(x)$ stops being unique when λ drops below $\frac{1}{4}$, and so the MFT lacks predictive power. For low-stickiness, when $\lambda > \frac{1}{4}$, the MFT is in good agreement with the simulations. However, one of the key predictions of the MFT, that a sharp transition to a no-flow regime occurs when λ becomes small enough (at least for 3 of the 4 sets of boundary conditions we investigated here), does not seem to be realised in our simulations. Indeed what seems to be happening is that the sharp transition has

been smoothed out, as we do not see any peaks or jumps in the flow rate variance or skewness, which we would expect to see if there was a transition. We suspect that this discrepancy is due to nontrivial correlations emerging between the particles, which the MFT does not take account of for obvious reasons. Alternatively, it could be the continuum assumption which has broken down, which in this case corresponds to the MFT assuming the presence of quasiparticles longer than the system length. As for the observed average density, for larger λ the density approaches the average of the boundary densities, and for small λ the density approaches 1 (which makes sense as the particles are very strongly attracted to each other, and so the system has a tendency to fill up); the exception to this is the case with extreme full/empty boundary conditions, although in this case one might argue that the particles are “sucked out” of the system so rapidly at the empty end that the system never really has a chance to fill up. It is also worth noticing that this extreme case is the only one in which the flow rate skewness does anything interesting; it is mostly positive, especially at low- λ , implying that most of the time the system is fairly static, but occasionally short-lived strong flows occur which end up causing most of the bulk flow.

Varying λ and Boundary Densities, Keeping the Average Density Constant

Another situation we can investigate has boundaries $(\rho_B, \rho_T) = (\rho_M + \frac{1}{2}\delta\rho, \rho_M - \frac{1}{2}\delta\rho)$ for some given ρ_M , where $\delta\rho$ and λ are varied. As before, I calculated flow rate moments and average densities, and the results are displayed in Figure 3. These calculations were performed with the same run parameters (system length etc) as above.

The MFT prediction for the mean flow is generally in good agreement with the numerics, except in the very sticky regime in which flow is very small. The simulations show no evidence of negative diffusion; rather the flow becomes critically slow for very sticky particles. The higher moments of the flow (e.g. variance, Figure 3 bottom left) do not show peaks, indicating that hard transitions aren't occurring. Finally (bottom right), the density is very close to the average of the boundary densities until drops below $1/4$, at which point the stickiness causes the system to fill.

Diffusion Coefficient Measurement

Let us again specify the boundary densities to be $(\rho_0, \rho_L) = (\rho_M + \frac{1}{2}\delta\rho, \rho_M - \frac{1}{2}\delta\rho)$ for some given ρ_M . This time we keep $\delta\rho$ relatively small, so that J varies approximately linearly with $\delta\rho$; thus if we calculate J for a series of small $\delta\rho$, we can perform linear regression

to find $D = \frac{\partial J}{\partial \delta\rho}|_{\delta\rho=0}$, the effective diffusion coefficient. Computing this for different (ρ_M, λ) combinations yields results that can be compared with Equation 3. In this setup we ran the simulation for 1.6×10^8 equilibration steps, followed by 10 sets of alternating measurement and relaxation runs, of lengths 8×10^7 and 1.6×10^7 steps respectively. We repeated the calculation with a system of half the size, and again found little difference between the two datasets, which gives us confidence that finite-size effects are small. We can of course obtain estimates of the confidence interval for our linear regression coefficient, and thus generate a standard error for D ; likewise we can obtain goodness of fit estimates for the regression. They are not included here for brevity, but they are in the additional materials.

Putting the MFT prediction and the actual numerical results together as we have done in Figure 4, we can compare and contrast. We see that MFT and simulation agree well for low stickiness, and both show the strange symmetry about $M = \frac{2}{3}$. For high stickiness, where the MFT prediction gives negative diffusion constant, the simulation generates a much increased density in the system. This takes M outside the negative- D regime of the MFT, and into slow, but positive D . The incorrectness of the MFT prediction suggests that some kind of nontrivial correlations have built up in this region, which makes sense as the coupling between particles has become stronger, whilst the density is middling, allowing that coupling to mean something. It is also worth noting that the discrepancy between intended density and actual density starts to become non-negligible here, which we can infer from how the originally rectangular grid of grey dots (indicating (ρ_M, λ) points where we obtained the data) has been deformed, to the extent that there is a big cluster of them in the observed minimum of the diffusion coefficient. Some of these anomalous densities are greater than the density of the denser reservoir to which the system is coupled; thus, the reservoirs involved are in some sense “unphysical” as the data suggests that they would immediately attempt to switch to a higher density, which given a constant volume constraint would imply a phase separation occurs; thus the numerical results aren’t fitting so well into the paradigm we were using to analyse them (flow between reservoirs with slightly different densities), so it’s little wonder the MFT is having trouble keeping up. Of course, we do not see the negative diffusion coefficient that naive application of MFT would suggest, because it would cause instability; instead, the diffusion coefficient just becomes very small, as the system becomes unresponsive to concentration gradients.

Flow Structure

Figure 5 shows the short-time-averaged local density as a function of space and time for a range of densities

and stickiness. A few observations:

When λ is extremely low (left), the medium consists of solid blocks surrounded by empty spaces containing a dilute gas of particles; as we alter the overall density, all that changes is the thicknesses of these blocks. Thus the breakdown of MFT is revealed as a decomposition into two regions, of low and high density, each of which allows similar flow rate. The MFT solution, which assumed intermediate density and gave negative diffusion constant, is revealed to be unstable. The case $\lambda = 1$ (right) is just excluded Brownian motion, and is included here for comparison. The most interesting images (centre) are those for the intermediate (ρ_M, λ) ; here we see a “lumpy” or “foamy” structure, in which small blocks of particles are being constantly created and destroyed whilst a rather minimal flow occurs across the system. The simulation did not show any hard phase transition as we vary ρ_M, λ ; rather, it seems that this “foamy” behaviour is part of a continuous range between the extremes, containing medium-range correlations between particles. Unfortunately, computing equal-time correlation functions to the accuracy required to draw conclusions about these correlations has proven to be extremely difficult, so we cannot find a quantitative description of the foam beyond the averages properties in Figures ???. In all images in Figure 5, long straight segments of white or black can be seen. These represent coherent motion at a characteristic velocity given by their gradient. There is nothing in the MFT to suggest what this velocity should be, and it is much smaller than the simulated system’s length divided by the elapsed time, $\frac{L}{T}$, thus it must be an emergent property arising from correlated motion of self-assembled regions of high- or low-density material.

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CONCLUSIONS

To conclude, we have solved a nonlinear model for self-interacting sticky particles diffusing in 1D. Although only the particles exhibit stickiness, the analytics suggest a symmetry between vacancy-type and particle-type flow at density of $\frac{2}{3}$, which is observed in the simulation. The flow exhibits a foamy pattern with intermediate time-and-space correlations. The continuum solution MFT is a good predictor of the bulk flow behavior of the SPM. The negative diffusion constant found in MFT at high stickiness indicates that the assumption of homogeneous density break down: thus the MFT predicts its own demise.

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ask about this ↴

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FIG. 2. Moments of flow rates and average overall densities observed when varying λ with fixed boundary densities (ρ_0, ρ_L) : Blue refers to $(\frac{2}{3}, \frac{2}{3})$, yellow to $(\frac{3}{4}, \frac{7}{12})$ (both with average density $\frac{2}{3}$); green to $(\frac{3}{4}, \frac{1}{4})$, red to $(\frac{99}{100}, \frac{1}{100})$ (with average density $\frac{1}{2}$). In the case of the mean flow we have an MFT prediction, indicated by the solid line.

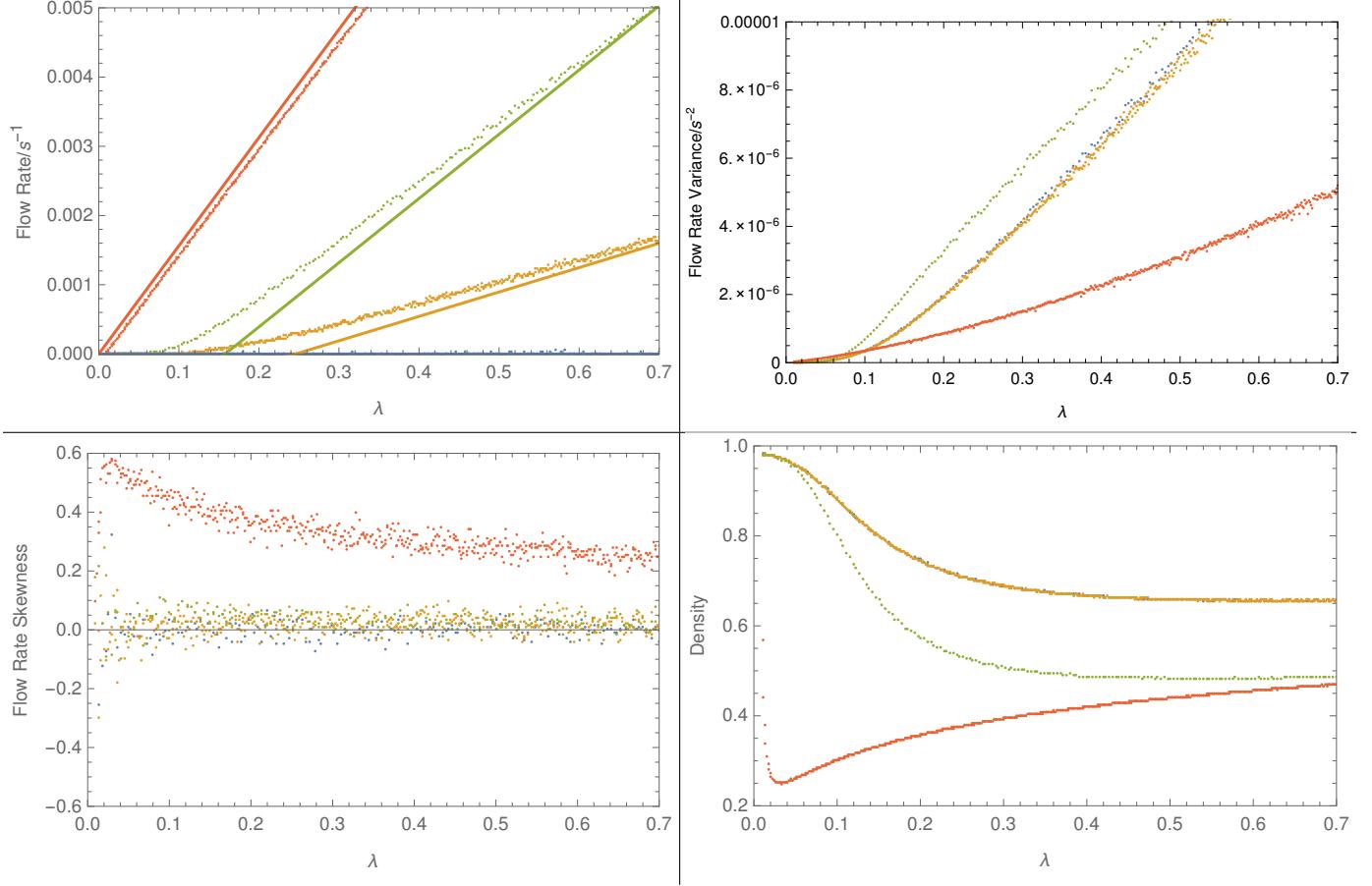


FIG. 3. Flow rate mean, flow variance and average overall densities observed when varying the difference $\delta\rho$ between the boundary concentrations $(\rho_B, \rho_T) = (\rho_M + \frac{1}{2}\delta\rho, \rho_M - \frac{1}{2}\delta\rho)$ and λ . I chose $\rho_M = \frac{1}{2}$, as this gives us the biggest range of $\delta\rho$ to investigate. The top left panel is the MFT prediction for the flow rate, whilst top right shows the observed mean flow rate. The measured flow skewness and kurtosis are not displayed here as both signals were small and noisy, and didn't show anything particularly significant.

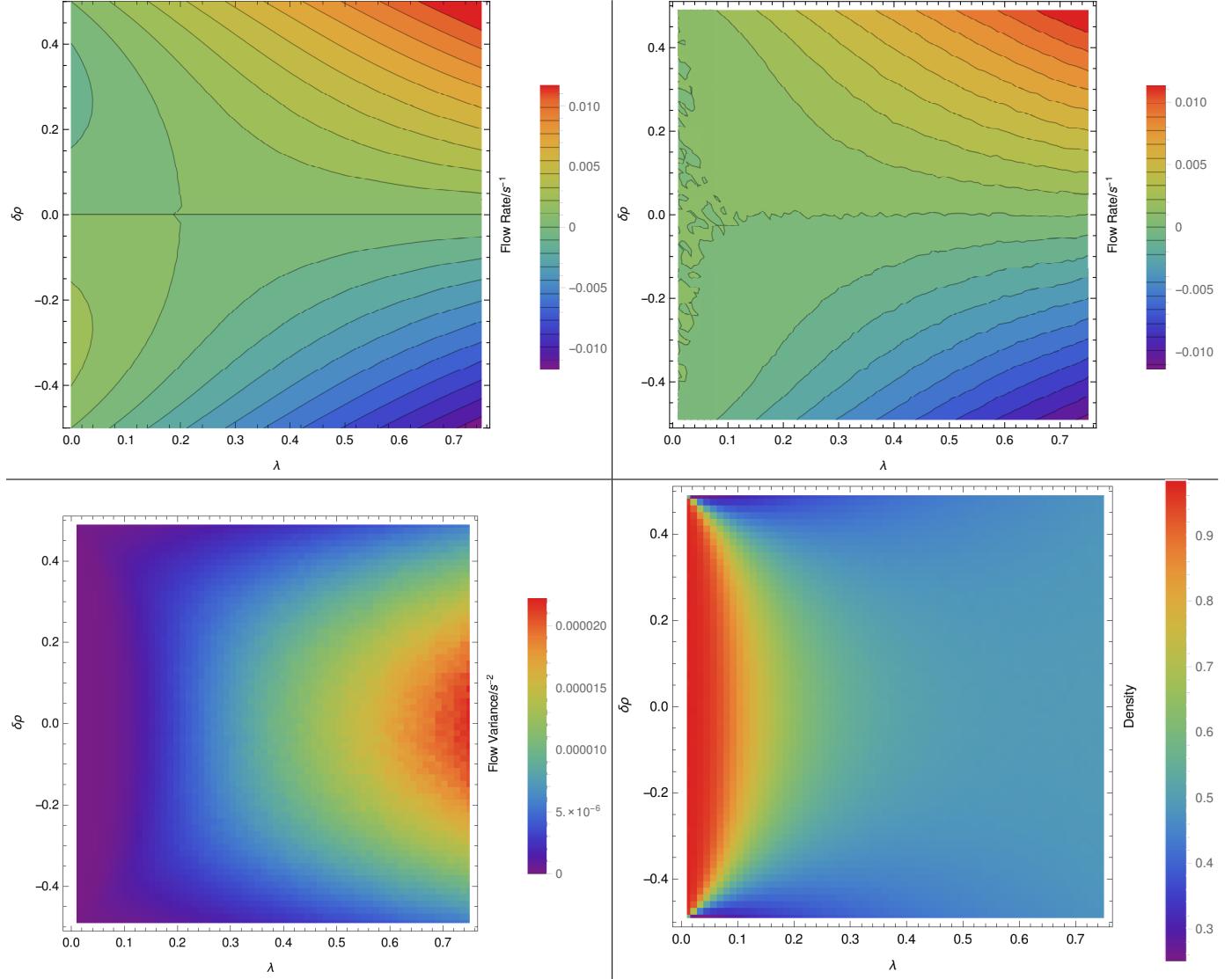


FIG. 4. The contour plot on the left shows the MFT prediction of the diffusion coefficient $D = \frac{\partial J}{\partial \delta \rho} \Big|_{\delta \rho=0}$ as a function of local density ρ_M and λ ; we are only plotting where $0 \leq D \leq 1.2$, other regions are shown in white, including the region in which $D < 0$, which would cause instabilities and so prevent a flow from actually occurring. On the right is our numerical calculation of $D(\rho_M, \lambda)$, with exactly the same plotting ranges. The dots indicate which points in (ρ_M, λ) we calculated D around, to give an impression of how the interpolation in the contour plot was done.

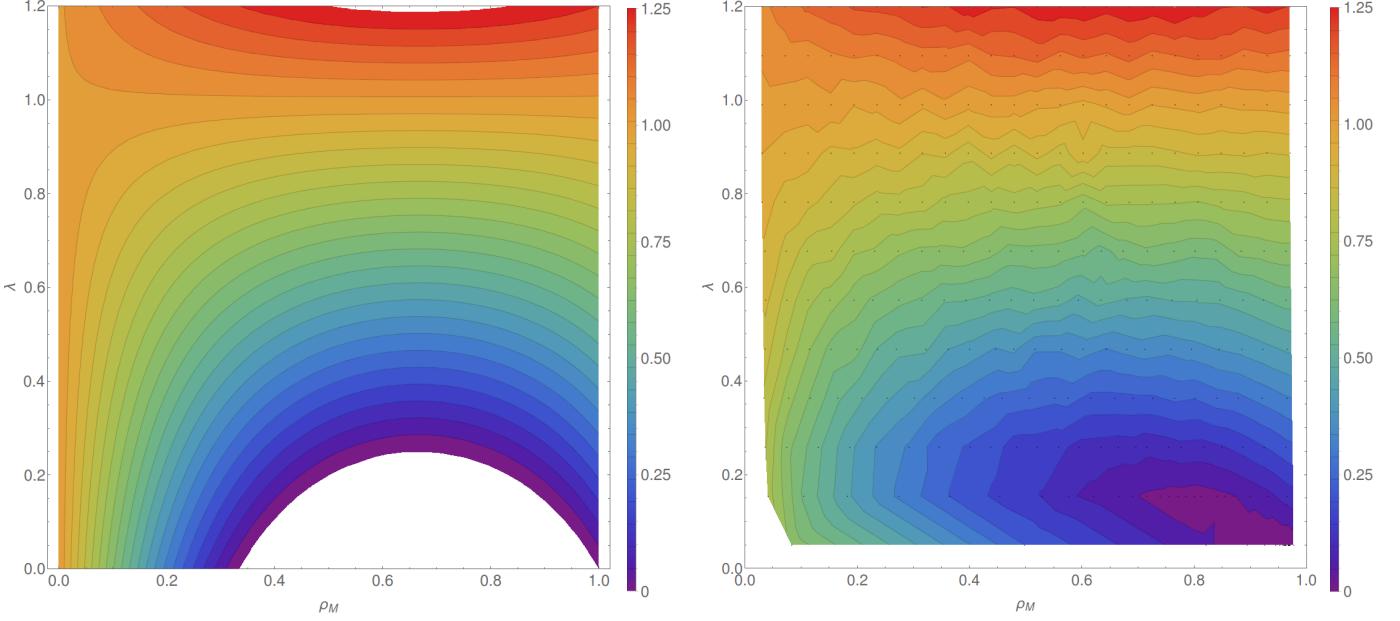


FIG. 5. The spacetime flow patterns, for the (λ, ρ_M) combinations indicated in the row and column headers. In each plot time runs along the x -axis, space along the y -axis. White represents full occupation, black empty, and grey shades partial occupation. The degree of occupation was calculated by taking the `KMCLib` record of a particular site's occupation (i.e. the Gillespie times at which the site changed occupation), assigning 0 and 1 to particles and vacancies respectively, linearly interpolating this and then integrating over times longer than a single Gillespie step but much shorter than the total time in question. In each case the total time elapsed is that taken by 10^6 Gillespie steps, and each short-time-average has been done over the total time divided by 508 (to produce square diagrams, as there are 508 active sites per simulation). Time has been rescaled this way in order to allow fair comparison of radically different λ -values.

