On The Diffusion of Sticky Particles in 1-D

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This is where I would write the abstract. This is probably best left until the end, as then I'll know what I'm actually summarising.

I. INTRODUCTION

There are a great many natural phenomena which involve the diffusion of small particles through solids; interface problems, such as the growth of a titanium dioxide layer on the surface of titanium metal exposed to air, are good examples [1]. If we wish to answer questions such as why these interfaces grow, or how quickly, we really need to understand how particles diffuse through crystal lattices, especially in the case when they interact with each other. In this paper we will introduce a very simple locally interacting exclusion model of this kind of diffusion, and we will explore the continuum-level implications of such a model.

We would intuitively expect that our titanium interface growth problem would involve the diffusion of oxygen atoms through titanium metal crystals. Once the concentration of oxygen is high enough, the medium becomes titanium dioxide. The oxygen atoms do this primarily by hopping between the interstitial sites between the titanium atoms. It is extremely energetically unfavourable for multiple oxygen atoms to occupy such a site, therefore to a good approximation we may regard these oxygen atoms as excluding each other from these sites, just like in ASEP [2, 3].

Next, let us assume that the lattice that the oxygen atoms move through is fairly rigid[4], and that the interactions between the oxygen atoms are quite short-ranged[5]. Finally, we should note that even though a problem like interface growth happens in three-dimensional space, the problem is rotationally and translationally invariant in a plane perpendicular to the direction of growth; therefore the interesting aspects of the problem are one-dimensional. Indeed, in anisotropic solids it is often the case that diffusion occurs much more rapidly along parallel chains than in other directions.

Putting these assumptions together, we are motivated to investigate the model described by the rates detailed in Figure I. It is essentially the symmetric exclusion model, only now the presence of an adjacent particle causes the hopping rate to change. We will henceforth refer to the model as the "sticky hopping model", or SHM.

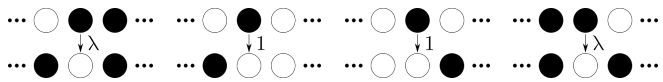

FIG. 1. Filled circles indicate particles, empty circles indicate empty sites (vacancies). Particles randomly move into adjacent vacancies with rate 1 (having rescaled time for notational convenience), unless there is a particle behind the position they're moving from, in which case they move with rate λ; $\lambda < 1$ represents attractive forces between particles, and $\lambda > 1$ repulsive.

II. MODEL PHENOMENOLOGY

The model described in Figure I is very simple, but numerical simulation shows that it is capable of a wide range of behaviours, such as those shown in Figures **??** and **??**. We will discuss these numerical results in more detail in Section **??**, but first let us try to predict the model behaviour using analytic means.

A. Mean-Field Theory Derivation

Let the spacing between lattice sites be a, τ_0 be the non-sticky hopping timescale and the time-averaged[6] occupation probability of the i^{th} lattice site be ρ_i. One may show that, in the mean-field approximation regime,

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

where $\zeta = 1-\lambda$ is to be regarded as a "stickiness parameter". Switching to the continuum limit by taking $a \to 0$, 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 which depends upon the local density.

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B. Continuum MFT Predictions

First let us consider some limits. As $\zeta \to 0$ (in other words, as the model becomes a simple exclusion model), $A \to 1$, so the MFT smoothly changes to match the known result. Likewise, in the dilute limit $\rho \to 0$, $A \to 1$, 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 $\rho \to 1$, $A \to \lambda$; this makes sense because we now have a dilute gas of vacancies, which hop with rate λ. Finally, we 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 $\frac{2}{3} - \frac{\sqrt{\zeta(4\zeta-3)}}{3\zeta} < \rho < \frac{2}{3} + \frac{\sqrt{\zeta(4\zeta-3)}}{3\zeta}$.

C. MFT Solutions

III. NUMERICAL RESULTS

A. Flow in a Block

B. Correlation Functions

[1] B. Tegner, L. Zhu, C. Siemers, K. Saksl, and G. Ackland, Journal of Alloys and Compounds **643**, 100 (2015).

[2] K. Sugden and M. Evans, Journal of Statistical Mechanics: Theory and Experiment **2007**, P11013 (2007).

[3] T. M. Liggett, *Interacting particle systems* (Springer-Verlag, Berlin, 1985).

[4] I.e. that the titanium atoms are quite tightly bound and don't move that much, which is reasonable as they are metal atoms in a metal.

[5] Any electrostatic forces should be rapidly screened by the metal, thus the main interaction should be via short-range electrostatics and electron sea distortion.

[6] Or ensemble-averaged, assuming ergodicity.