Adsorption and desorption in confined geometries: A discrete hopping model

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Abstract. We study the adsorption and desorption kinetics of interacting particles moving on a one-dimensional lattice. Confinement is introduced by limiting the number of particles on a lattice site. Adsorption and desorption are found to proceed at different rates, and are strongly influenced by the concentration-dependent transport diffusion. Analytical solutions for the transport and self-diffusion are given for systems of length 1 and 2 and for a zero-range process. In the last situation the self- and transport diffusion can be calculated analytically for any length.

1 Introduction

Diffusion in confined geometries is ubiquitous in nature, for example in biological cells [1,2]. An important case is diffusion in micro-porous materials, such as zeolites and metal-organic frameworks (MOFs) [3]. Because of their structure on the molecular scale and large surface area, they are ideally suited for e.g. catalysis and particle separation. Micro-porous materials occur naturally, but can also be made in the laboratory. New fabrication techniques have led to a large increase in available materials, with a great diversity in possible structures [4–6]. Many applications require a proper understanding of how particles diffuse in these materials. Thanks to recent advances a detailed experimental view of diffusion in micro-porous materials is now available [7]. A theoretical analysis is notoriously difficult due to the complex interactions involved. Progress has been made by advanced molecular dynamics simulations [8–10], or via coarse-grained stochastic models in continuous space [11–16] or on a lattice [17,18]. In a recent paper [19] we introduced a lattice model that provides an intuitive interpretation of the role of interactions upon the transport and self-diffusion. By fitting only equilibrium properties, good agreement was found with experimental results of methanol diffusion in MOF ZIF-8 [20].

In this work, we discuss the adsorption and desorption kinetics of this model. The rates at which particles are absorbed/desorbed from the material are of crucial importance for many applications [21]. Particle interactions have a large influence on

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The system, shown between dotted lines, consists of cavities connected by narrow windows. On the boundaries the system is connected to cavities with an uncorrelated equilibrium distribution. a) The transport diffusion is measured under a steady concentration gradient $\mu_l \neq \mu_r$, in first order around equilibrium. b) The self-diffusion is measured in equilibrium ($\mu_l = \mu_r = \mu$), where a concentration gradient of labeled (green) particles is introduced.

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The influence of interactions is therefore studied in detail.

The paper is organized as follows. We introduce the model in Sect. 2. In Sect. 3 we present analytical expressions of the transport and self-diffusion coefficients. Transport diffusion plays a crucial role here, since adsorption/desorption is the result of mass transfer in response to a concentration gradient. For certain parameters the model reduces to a zero-range process. In this case it is always analytically solvable. In Sect. 4 the adsorption and desorption kinetics of the model is discussed. Our main conclusions are presented in Sect. 5.

2 The model

The system we consider is a one-dimensional array of $L$ cavities, each one connected to its nearest neighbours. The outer left and right cavities are connected to reservoirs, allowing particles to enter/leave the system. A sketch is shown in Fig. 1. Particles can move between the cavities by passing through the narrow channel in between. This type of system is a paradigmatic model for the study of diffusion under confinement [23–27]. Due to the narrow passages, the time spent by the particles in a cavity before moving to one of its neighbours is considered much larger than the relaxation time inside a cavity. This is a common assumption in the modeling of such structures [28–32]. Consequently, this separation of time-scales allows for a coarse graining of the intra-cavity degrees of freedom [33], and the state of cavity $i \in \{1, L\}$ is characterized solely by the number of particles $n_i$ it contains. The interactions of $n$ particles in a cavity are described by the equilibrium free energy

$$F(n) = U(n) - TS(n),$$

(1)

with $U(n)$ and $S(n)$ the average energy and entropy respectively. The system is at constant temperature $T$. When the system is in equilibrium with a reservoir at chemical potential $\mu$, the probability to find $n$ particles in any cavity is:

$$p_n^\text{eq}(\mu) = Z(\mu)^{-1}e^{-\beta[F(n) - \mu n]},$$

(2)

with $Z(\mu)$ the normalization constant. Contributions to $F(n)$ come from particle-particle and particle-cavity interactions. We assume that there is no interaction between particles residing in different cavities. This is a good quantitative approximation