Inverted regions induced by geometric constraints on a classical encounter-controlled binary reaction

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The efficiency of an encounter- controlled reaction between two independently- mobile reactants on a lattice is characterized by the mean number of steps to reaction. The two reactants are distinguished by their mass with the "light" walker performing a jump to a nearest- neighbor site in each time step, while the "heavy" walker hops only with a probability p; we associate p with the "temperature" of the system. To account for geometric exclusion effects in the reactive event, two reaction channels are specified for the walkers; irreversible reaction occurs either in a nearest- neighbor collision, or when the two reactants attempt to occupy the same site. Lattices subject to periodic and to confining boundary conditions are considered. For periodic lattices, depending on the initial state, the reaction time either falls off monotonically with p or displays a local minimum with respect to p; occurrence of the latter signals a regime where the efficiency of the reaction effectively decreases with increasing temperature. Such behavior can also occur when one averages over all initial conditions, but it disappears if the jump probability of the light walker falls below a characteristic threshold value. Even more robust behavior can occur on lattices subject to confining boundary conditions. Depending on the initial conditions, the reaction time as a function of p may increase monotonically, decrease monotonically, display a single maximum or even a maximum and minimum; in the latter case, one can identify distinct regimes where the above- noted inversion in reaction efficiency can occur. We document both numerically and theoretically that these inversion regions are a consequence of a strictly classical interplay between excluded volume effects implicit in the specification of the two reaction channels, and the system's dimensionality and spatial extent. We also discuss briefly how the above behavior changes when a certain number of connections between lattice sites are randomly rewired. Our results highlight situations where the description of an encounter- controlled reactive event cannot be described by a single, effective diffusion coefficient. We distinguish between the inversion region identified here and the Marcus inverted region which arises in electron transfer reactions.