

MAR11-2011-020272

Abstract for an Invited Paper  
for the MAR11 Meeting of  
the American Physical Society

### **Crowding effects on protein association**

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The cell cytoplasm is a dense environment where the presence of inert cosolutes can significantly alter the rates of protein folding and protein association reactions. These crowding effects can either increase or decrease the rates of association reactions (or protein folding) depending on the nature of the crowding agents and the type of reaction. Our work aims to obtain a quantitative understanding of crowding effects. We present the first kinetic study of the effect of hard sphere crowding agents on protein association reactions where reactants and crowding agents are both hard spheres. If every collision results in a reaction, crowding always decreases the reaction rate but if the probability of a reaction is low then crowding increases the reaction rate. We find that the thermodynamics of crowding are relatively insensitive to interactions between the crowding agents suggesting that the hard sphere model of crowding agents has a surprisingly large regime of validity, and should be sufficient for a qualitative understanding of the thermodynamics of crowding effects.