Experimental measurement of binding energy, selectivity and allostery using fluctuation theorems

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Thermodynamic bulk measurements of binding reactions rely on the validity of the law of mass action and the assumption of a dilute solution. Yet important biological systems such as allosteric ligand-receptor binding, macromolecular crowding, or misfolded molecules may not follow these assumptions and require a particular reaction model. In this talk we introduce a fluctuation theorem for ligand binding and an experimental approach using single-molecule force-spectroscopy to determine binding energies, selectivity and allostery of nucleic acids and peptides in a model-independent fashion. A similar approach could be used for proteins. This work extends the use of fluctuation theorems beyond unimolecular folding reactions, bridging the thermodynamics of small systems and the basic laws of chemical equilibrium.