Non-Equilibrium Umbrella Sampling Applied to Force Spectroscopy

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Physical systems often respond on a timescale which is longer than that of the measurement. This is particularly true in soft matter where direct experimental measurement, as for example in force spectroscopy, drives the soft system out of equilibrium and provides a non-equilibrium measure. Here we describe a rigorous method that allows us to determine equilibrium physical quantities from non-equilibrium measurements. This method is based upon umbrella sampling, a technique used in statistical mechanics to generate a biased ensemble so as to better describe equilibrium properties; here the method is extended to non-equilibrium ensembles and applied in real experiment - not in silico. Specifically we show that experimental force spectroscopy of soft systems provides an already-biased ensemble of non-equilibrium force measurements: measurement of that bias and its extraction from an ensemble average leads to equilibrium average properties. We demonstrate this with a model experimental system: a colloid fluctuating in a time-varying optical trap. We also show this for simulated force spectroscopy on a complex soft molecule -- a piston rotaxane.