

Direct measurement of single molecular interaction free energies at solid/liquid interfaces based on non-equilibrium force spectroscopy

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Unraveling the complexity of the macroscopic world based on molecular level details relies on understanding single molecule interactions and their scaling towards integral interactions at the meso- and macroscopic scale. Here, I will discuss how one can measure the interaction free energy of single interacting functional groups with surfaces at a variety of solid/liquid interfaces. Also, I will show how these interactions scale with the number density towards the macroscopic level [1, 2], where a large number of these bonds interact simultaneously.

In particular, we developed a synergistic experimental approach combining Surface Forces Apparatus (SFA) experiments and single molecule force spectroscopy (SMFS). Equilibrium SFA measurements scale linearly with the number density of a model acid-base bond at an interface, providing acid-amine interaction energies of 10.9 ± 0.2 kT. Using Bell-Evans theory together with Jarzynski's equality, we can demonstrate how a set of single molecule interaction forces measured by SMFS similarly converges to an interaction energy of 11 ± 1 kT, with unbinding energy barriers of $25 \text{ kT} \pm 5 \text{ kT}$. This demonstrates excellent predictive power of our newly developed scaling approach.

In addition to acid/base interactions, we tested a number of other bonds including hydrophobic, ligand-receptor, mussel-peptide/surface and metal/polymer [2] bonds with our model and find that our model is widely applicable. In this context, we will discuss in detail how single molecule unbinding energy landscapes can be utilized to predict scenarios where a large number of molecules simultaneously interact, giving rise to both macroscopic equilibrated and non-equilibrated interaction energies during adhesive failure. As such, our experimental strategy provides a unique framework for the molecular design of novel functional materials through predicting of large-scale properties such as adhesion, self-assembly or cell-substrate interactions based on experimentally determined single molecule energy landscapes.

[1] S. Raman et al. in *Nature Communications*, 5 (2014), 5539.

[2] T. Utzig et al. in *Langmuir*, 31(9) (2015), 2722.