TEARING MOLECULAR CLUSTERS APART LIMB FROM LIMB TO COMPUTE THEIR SURFACE TENSION

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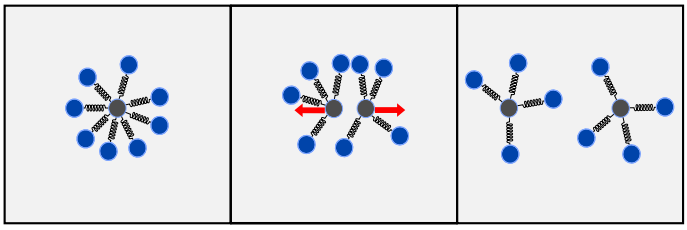
The surface tension of a small, loosely bound cluster of molecules has a very specific meaning, and a firm theoretical basis, in spite of the cluster's lack of a distinct geometry. It is an expression of the relative stability of clusters in an equilibrium vapour, and of the rate of formation of stable droplets from a metastable vapour according to the nonequilibrium statistical mechanics of the nucleation process.

I shall describe a computational method for determining the surface tension of clusters of a variety of molecules, using a nonequilibrium molecular dynamics method involving 'mitosis'. We pull a cluster apart into two subclusters using external guiding forces, and a set of realisations of the process allows us to relate the mechanical work performed to the free energy of separation, using the Jarzynski equality [1]. The free energy can then be converted into a difference between the surface tensions of the parent and daughters. Clusters of 2^n molecules can be divided into monomers using n mitosis steps and the size dependence of the surface tension extracted.

We have pulled apart single species clusters of argon [2] and of water [3]; binary clusters of sulphuric acid with water [4]; and most recently clusters of the ionic material caesium hydroxide [5]. The method is particularly suitable for liquid-like clusters where harmonic oscillator approximations are not appropriate.

The method produces values consistent with other studies based on equilibrium simulations. Little attention needs to be given to imposing a cluster definition, and the reference case of separated monomers is natural for the purposes of assessing the cluster stability.

The sketch illustrates the tearing apart of a cluster of molecules (blue) 'limb from limb' using the motion of guide particles (grey) attached using harmonic bonds.



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