Minimum Free Energy Path by the String Method

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A computational technique is proposed which combines the string method [1] with a sampling technique to determine minimum free energy paths (MFEP) [2]. The technique only requires to compute the mean force and another conditional expectations locally along the string, and therefore can be applied even if the number of collective variables kept in the free energy calculation is large. The theoretical background of the technique as well as its computational aspects are discussed in details.

As an illustration, the nucleation path of a phase transition in the two dimensional Ising model under different conditions is studied using the MFEP approach [3]. The key idea is to work in collective variables, consisting of block of spins, which allow for a continuous approximation of the collective variables state-space. The string method computes the minimum free energy path in this collective variables space, which is shown to explain the mechanism of the phase transformation (in particular, an approximation of its committor function, its free energy and its transition state). The approach is used to analyze the phase transition in the Ising model with imposed boundary conditions and in a periodic system under an external field of increasing magnitude. In each case, the mechanism of the phase transformation is elucidated.

[1] E, W., Ren, L., Vanden-Eijnden, E. Phys. Rev. B 66, 052301 (2002)
[2] L.Maragliano, A.Fischer, E.Vanden Eijnden, and G.Ciccotti, "String method in collective variables: minimum free energy paths and isocommittor surfaces", J.Chem.Phys., 125, 024106, (2006)
[3] M.Venturoli, E.Vanden-Eijnden, and G.Ciccotti, "Kinetics of phase transitions in the two-dimensional Ising models studied with the string methods", J.Math.Chem. 45, 188, (2008)