Free energy profile along a discretized reaction path via the hyperplane constraint force and torque

Konstantin N. Kudin and Roberto Car

Department of Chemistry, Princeton University
Princeton, NJ, 08544, USA

We derive a convenient computational approach for evaluation of the free energy profile (FEP) along some discretized path defined as a sequence of hyperplanes.[1] A hyperplane is fully specified by any of its point and a tangent vector. The FEP is obtained as an integral of two components. The translational component of the free energy is computed by integrating the hyperplane constraint force. The rotational component is evaluated via the hyperplane torque. Both ingredients – the constraint force and the hyperplane torque – are evaluated on each hyperplane independently. The integration procedure utilizes a set of reference points defining a point of rotation on each hyperplane, and these points can be chosen before or after the sampling takes place. A shift in the reference points redistributes the FEP contributions between the translational and rotational components. For systems where the FEP is dominated by the potential energy differences, reference points residing on the minimum energy path present a natural choice. We demonstrate the validity of our approach on several examples. In each case, the rotational component of the FEP represents a sizable contribution to the total FEP, so ignoring it would yield clearly incorrect results.

[1] K. N. Kudin and R. Car, J. Chem. Phys. **122**, 114108 (2005).