

On-the-Fly Free-Energy Parameterization (OTFP)

Basis-function expansion

$$\tilde{F}(z) = \sum_k \lambda_k \phi_k(z)$$

Minimize

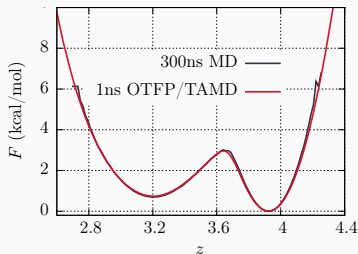
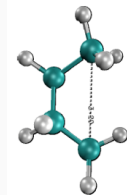
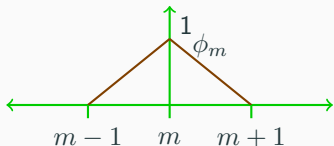
$$\frac{\partial E}{\partial \lambda} = 0 \rightarrow A\lambda = b \rightarrow \lambda = bA^{-1} \rightarrow \tilde{F}(z)$$

Error estimate

$$E(\lambda) = \left\langle \sum_j \left[\kappa[z_j - \theta_j(\mathbf{x})] - \frac{\partial \tilde{F}(z)}{\partial z_j} \right]^2 \right\rangle_{\text{TAMD}}$$

$$A_{nm} = \frac{1}{2} \left\langle \sum_i \frac{\partial \phi_m(z)}{\partial z_i} \frac{\partial \phi_n(z)}{\partial z_i} \right\rangle_{\text{TAMD}}$$

$$b_m = \left\langle \sum_i \frac{\partial \phi_m(z)}{\partial z_i} \kappa[z_i - \theta_i(\mathbf{x})] \right\rangle_{\text{TAMD}}$$



CFA and E. Vanden-Eijnden *Chem Phys Lett* 547:114 (2012)