Recent simulation methods for resolving molecular details in thermodynamics and kinetics

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Temperature-Accelerated MD

Maragliano and Vanden-Eijnden, *Chem Phys Lett* **426**:168 (2006)

Extended potential energy: $U(\boldsymbol{x}, \boldsymbol{z}) = V(\boldsymbol{x}) + \frac{1}{2}\kappa \sum_{j=1}^{M} [\theta_j(\boldsymbol{x}) - z_j]^2]$

Dynamics of configurational variables $\boldsymbol{x}$ ("restrained MD"):

$$m_i \ddot{x}_i = -\frac{\partial V(\boldsymbol{x})}{\partial x_i} - \kappa \sum_{j=1}^{M} [\theta_j(\boldsymbol{x}) - z_j] \frac{\partial \theta_j}{\partial x_i} + \text{thermostat @ } \beta$$

Dynamics of auxiliary variables $\boldsymbol{z}$ with enforced separation of time-scales:

$$\bar{\gamma}\bar{m}_j \dot{z}_j = \kappa [\theta_j(\boldsymbol{x}) - z_j] + (\text{noise @ } \bar{\beta}) \approx -\frac{\partial F_\kappa}{\partial z_j} + \text{noise}$$

$\boldsymbol{z}$ responds to free energy like $\boldsymbol{x}$ responds to potential energy.
Taking $\bar{\beta} < \beta$ ($\bar{T} > T$) $\Rightarrow$ enhanced sampling in a chosen CV-space.