Free energy analyses on cluster deformations by cumulant mechanics

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We have formulated extended dynamics that describe fluctuation around classical variables in terms of cumulants and applied these methodologies to quantal and statistical mechanics and dynamics [1-2]. In this study, we propose a method for the variational determination of free energy within cumulant mechanics. Within second-order approximation to cumulant variables, the free energy functional for the one-dimensional case is given as

$$F=\frac{1}{2m}\left(p_0^2+\sigma h\right)-\frac{k_BT}{2}\left(1+\ln\left(2\pi\sigma\right)\right)+\int\frac{dq}{\sqrt{2\pi\lambda}}\exp\left[-\frac{\left(q-q_0\right)^2}{2\lambda}\right]V\left(q\right)-\frac{k_BT}{2}\left(1+\ln\left(2\pi\lambda\right)\right)$$

where q (q_0) and p (p_0) are the classical position and momentum and σ and λ are the second-order cumulant variables for position and momentum, respectively. h is the Planck constant originated from the statistical normalization relation. Free energy minima are optimized as a function of q_0, p_0, λ, and σ. This method can be easily generalize to treat multi-dimensional many-body systems.

For the 7 particle Morse cluster, where particles interact with the inter-particle Morse potential $V_M\left(r_{ij}\right)=\exp\left(-2\left(r_{ij}-R_e\right)\right)-\exp\left(-\left(r_{ij}-R_e\right)\right)$, free energy landscape along the two-dimensional reaction coordinates (RCs; distances between 1 and 3, r_{13}, and 1 and 7, r_{17} are chosen) for a deformation of cluster from PBP structures (left-upper and right-lower regions) to COCT structure (right-upper region), where we set temperature as k_BT=0.01 (/unit) and mass as m=1000, is given in Figure 1. Free energy barrier from the PBP structure is 0.41 (/unit), which is in good accordance with that obtained by conventional method such as metadynamics. This method requires less computational cost than the ordinary molecular dynamics simulations indicating promising method to evaluate free energy surface s for given systems.

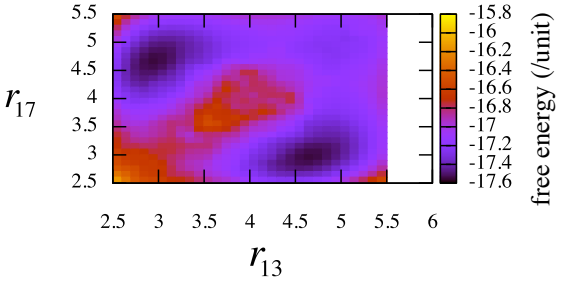

Figure 1 Free energy landscape along r_{13}-r_{17} axis

[1] Y. Shigeta et al., *JCP* **125**, 244102(2006) .
[2] Y. Shigeta, *BCSJ* **82**, 1323 (2009).