Coarse-graining of Feynman Path Integrals in Statistical Mechanics

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The imaginary time Feynman path integral formalism for quantum statistical mechanics provides a way of understanding the nuclear quantum effects in complex condensed matter systems. Several numerical path integral based methods such as path integral molecular dynamics (PIMD), path integral Monte Carlo (PIMC), centroid molecular dynamics (CMD), and ring polymer molecular dynamics (RPMD) have been developed based on the quantum-classical isomorphism in which a completely classical "ring polymer" can be used to represent each quantum particle. We have recently been addressing two important problems in the area of path integral methodologies. First, despite the success of the previously mentioned numerical methods, path integral simulations are more computationally expensive than classical ones due to the presence of multiple quasi-classical "beads" in the isomorphic ring polymer. By combining the quantum-classical isomorphism and a systematic coarse-graining (CG) methodology, we have developed a many-body formalism of the coarse-graining of path integrals (CG-PI) approach and have devised a methodology based on the exact CG-PI theory called numerical CG-PI (n-CG-PI). Due to the CG representation of the ring polymers, which greatly decrease the number of degrees of freedom to be considered, it is shown that n-CG-PI can quantitatively capture the structural features of liquids compared against the exact PIMD results with only computational resources that an equivalent classical MD simulation would use. To expand on the many-body CG-PI theory work, we have also worked out a further refinement of the analytical CG-PI theory to include many-body interaction effects in the derivation. Additionally, a more sophisticated algorithm to numerically calculate the effective CG potential is currently being developed. The CG-PI theory, both in exact and approximate forms, further provides an important reductionist conceptual perspective to understand equilibrium quantum systems at finite temperature. A second project concerns the RPMD method, which seeks to approximate real time quantum dynamics. RPMD has been known to suffer from a "resonance problem" in which non-physical peaks appear in the RPMD calculated vibrational spectra. This arises when the frequencies of the higher order normal modes of the ring polymer are similar to those of the physical system, and it is an unphysical artifact of the method. To better understand the behavior of RPMD dynamics, we have carried out an analysis that utilizes the generalized Langevin equation (GLE). Such a formalism uses a familiar system-bath motif, and is shown to reproduce the general behavior of RPMD time correlation functions. The analysis also helps to explain why RPMD deviates from the exact quantum results for simple one-dimensional anharmonic oscillator systems.