Mean-Field Dynamics of Curvilinear Centroids: Tackling the Curvature Problem

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Popular path-integral methods for approximating the quantum dynamics of condensed-matter systems all encounter problems when simulating infra-red absorption spectra. In particular, ring-polymer molecular dynamics (RPMD) exhibits spurious resonances with the internal ring-polymer modes [1,2], and its thermostatted variant TRPMD produces artificially broadened line-shapes when subjected to a white-noise thermostat [3]. The recently proposed coloured-noise TRPMD yields improved predictions in the stretch region, at the expense of the low-frequency part of the spectrum [4]. Centroid molecular dynamics (CMD) suffers from no such artefacts, but runs into the *curvature problem* at sufficiently low temperatures, resulting in artificial red-shifts and line-shape deterioration [2]. We present a new path-integral method that generalises the mean-field centroid dynamics of CMD to *curvilinear* coordinates. A judicious choice of these coordinates allows us to eliminate the curvature problem in our test systems, ranging from two-dimensional models to q-TIP4P/F liquid water and ice [5]. We present the results of our simulations alongside exact quantum predictions when such are available, and approximate wavefunction-based calculations otherwise. We show that the method performs well over a broad range of temperatures and discuss its generalisations to other systems.

References

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