Real-time dynamics from imaginary-time path-integrals: Theory and practice

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Imaginary-time path-integrals or 'ring-polymers' are a long-established practical technique for simulating quantum Boltzmann statistics. More recently, they have also been used to simulate real-time dynamics, using the centroid molecular dynamics (CMD) and (thermostatted) ring-polymer molecular dynamics ((T)RPMD) methods. Here, we show that the theoretical basis of CMD and RPMD is a classical dynamics which arises when the exact quantum dynamics is represented using path-integrals and is coarse-grained to make it a smooth and differentiable function of imaginary-time. This ‘Matsubara’ dynamics cannot be used as a practical method (because of a severe sign problem), but can be used to critique and refine heuristic methods such as CMD and RPMD, which turn out to be approximations to Matsubara dynamics that avoid the phase. In particular, we will show how to extend quantum simulations of the infrared spectrum of liquid water and ice to lower temperatures (150 K) than hitherto possible.