3.3. Validating the implementation

We employ a set of tests to validate the correct implementation of the CENT method. One way of testing whether CENT provides reliable energetics and dynamics is based on performing a *NVE* simulation with a molecular dynamics integrator that is time reversible. We use the velocity Verlet algorithm for this task. Since our implementation of CENT provides atomic forces based on exact, analytical derivatives of the potential energy, the sum of the kinetic and potential energy is conserved along the trajectory.

To validate the implementation of the stress tensor we would have to perform *NPH* dynamics. Unfortunately, available integrators for such ensembles [42,43], where the equations of motions for the reduced atomic coordinates and cell variables are coupled, are not time reversible. Hence, we routinely employ an alternative method to validate our implementation based on a path integral scheme with sufficiently small step size $d\vec{r}$. Conservative force fields $\vec{F}$ that are derived from the negative gradient of a potential E, $\vec{F} = -\vec{\nabla}E$, lead to zero net work W done by the force when moving a system through a trajectory in a closed loop C: $W = \oint_C \vec{F} \cdot d\vec{r} = 0$. Equivalently, any path taken from configuration A to B must lead to the same work independent of the path: $W = \int_A^B \vec{F} \cdot d\vec{r} = -\int_A^B \vec{\nabla}E \cdot d\vec{r} = E(A) - E(B)$. We use multiple randomly generated trajectories that involve the displacement of all atoms and cell parameters to ensure that the path integral is sufficiently converged.