1. Introduction

Metal organic frameworks (MOFs), an important class of porous systems because of their easily tunable physical and chemical properties, are envisioned to play a key role in adsorption based technologies. Since, adsorption and desorption processes involve exchange of energy, the heat capacity is an important property of interest. Unfortunately, it is not straightforward to calculate since it is heavily influenced by the quantum nature of nuclei. We present an efficient and accurate protocol for the calculation of heat capacity which should facilitate the identification of structure function relations for thermal properties.

2. State of the art method

The heat capacity at constant pressure is defined as:

\[ C_p = \frac{\partial^2 \ln \Delta(N, P, \beta)}{\partial \beta^2} \]

The quantum partition function can be calculated classically through the path integral isomorphism:

\[ Z = \text{tr}(e^{-\beta H}) = \int dq dp \ e^{\beta H(q,p)} + O(P^{-2}) \]

The classical Hamiltonian is known as the second ordered ring polymer Hamiltonian since it is made of \( P \) replicas of the physical system. The thermodynamics of the classical Hamiltonian at \( P \) times the temperature is same as that of the quantum system for large \( P \).

As the temperature decreases the number of replicas also increases making the simulations > 500 times more expensive than classical MD.

3. New developments (I)

A more effective Hamiltonian for which the error goes as \( 1/P^4 \) can be derived

\[ Z = \text{tr}(e^{-\beta H}) = \int dq dp \ e^{-\beta H^{(2)}} + O(P^{-4}) \]

The Hamiltonian however depends on high order derivatives of the potential for which the forces depend on the Hessian. We develop finite difference expressions for the force:

\[ \frac{\partial f}{\partial q} = \lim_{\epsilon \to 0} \left[ f(q + \epsilon M^{-1} f(q)) - f(q) \right] e^{-1} \]

4. New developments (II)

If the potential can be expressed as a slow and a fast term, the slow term can be extrapolated from a smaller number of replicas and integrated with a larger timestep.

5. Validation

The method was validated on the constant volume heat capacity of a harmonic model of a paracetamol crystal for which the exact result is known.

For \( P=96 \) beads the high order scheme converges to the exact result. The standard scheme gives errors ~ 300 % at low T.

6. Results

The method was used to study the thermal properties of MOF-5 with 100 molecules of CH\(_4\). The interactions were modelled by an ab initio based forcefield called YAFF. The cheap bonds and angle terms were calculated for 64 replicas while the expensive long range interactions were calculated for 16 replicas.

The second order scheme would have required \( P \sim 512 \) making it more than two orders of magnitude more expensive.

References

1. Kapil et. al. JCP 2016
2. Kapil et. al. JCP 2016

This work was done in a collaboration with the group of Prof. Veronique Van Speybroeck at the Centre for Molecular Modeling, Ghent.