Quantum Statistical Mechanics with Nested Sampling

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In the path integral formulation, the quantum partition function for a single dimension is expressed asymptotically as

\[ Z(\beta) = \lim_{P \to \infty} Z_P(\beta) \]

where

\[ Z_P(\beta) = \left( \frac{mP}{2\pi \beta \hbar^2} \right)^{\frac{P}{2}} \int dx_1 \ldots dx_P \times \exp \left( -\beta \sum_{s=1}^{P} \left[ \frac{mP}{2\beta \hbar^2} (x_{s+1} - x_s)^2 + P^{-1} V(x_s) \right] \right). \]  (1)

The partition function \( Z_P(\beta) \) corresponds to the classical partition function for \( P \) classical systems which do not interact except that they are connected by springs, with spring constant proportional to \( T^2 \). Although much impressive work has been done to develop methods for sampling the configurational probability distribution for a system of \( P \) such classical systems, at present there is no generally applicable methodology for calculating \( Z_P(\beta) \) for atomistic systems as an explicit function of \( \beta \). The aim of this project is to develop such a methodology for \( P \) copies of \( N \) particles in 3 dimensions, in order to allow the direct application of the path integral formulation of quantum statistical mechanics to real systems.

The partition function \( Z_P(\beta) \) may be written as an integral over the joint density of states

\[ Z_P(\beta) = \left( \frac{mP}{2\pi \beta \hbar^2} \right)^{\frac{P}{2}} \int dE_1 dE_2 \frac{g(E_1, E_2|P)}{\beta} \exp \left( -\left[ \frac{E_1}{\beta} + \beta E_2 \right] \right) \]

where

\[ E_1 = \frac{mP}{2\hbar^2} \sum_{s=1}^{P} (x_{s+1} - x_s)^2, \quad E_2 = P^{-1} \sum_{s=1}^{P} V(x_s) \]
and

\[ g(E_1, E_2|P) = \int dx_1 \ldots dx_P \delta (E_1(x) - E_1) \delta (E_2(x) - E_2). \]

It has recently been shown that Nested Sampling can be used to calculate the configurational density of states for a single classical system. This project will build on this advance to calculate the joint density of states \( g(E_1, E_2|P) \) for a system of \( P \) classical systems by retrospectively sampling from the output of a single classical nested sampling calculation, thereby bypassing the need for further expensive configuration space sampling for \( P > 1 \). This will enable the efficient calculation of quantum partition functions as explicit functions of \( \beta \), and allow the discovery of quantum phases and quantum phase transitions from first principles.