

General approach to compute the isothermal-isobaric partition function using Nested Sampling

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Abstract #: 399

Introduction

In the context of atomic simulation Nested Sampling (NS) is a powerful configuration sampling technique which allows for the calculation of the partition function and thermodynamic properties at essentially any temperature after the NS simulation is complete. NS was first demonstrated in the context of atomic simulation in 2010 by Partay et al.[1], in which they demonstrated the computation of the canonical (NVT) partition function from NS. Subsequently, NS has been used for the study of protein energy landscapes [2], and free energy of liquids and solids [3,4,5]. In this work we will show how NS can be adapted to compute the isothermal-isobaric (NPT) partition function in general.

Nested Sampling – Isothermal-Isobaric Partition Function

The isothermal-isobaric (NPT) system has the conditions of constant particle count (N), pressure (P), and temperature (T). The excess portion of the NPT partition function can be written as

$$\Delta_{Ex} = \int_0^{\infty} V^N dV \int \Omega_V(E) dE e^{-\beta H}$$

where H is the enthalpy given by

$$H = E + PV$$

and $\beta = (kT)^{-1}$ where k is the Boltzmann constant.

The partition function can then be reduced to a density of enthalpy states form given by

$$\Delta_{Ex} = \sum_i g(H_i) e^{-\beta H_i}$$

where $g(H_i) = \sum_j V_j^N \Omega_{V_j}(E_j)$, assuming $E_j + PV_j = H_i$

The NS algorithm can then be applied to compute the NPT partition function by making a top down sweep of enthalpy space.

Basic Nested Sampling Algorithm To Compute The Isothermal-Isobaric (NPT) Partition Function:

1. Select the pressure value
2. Sample the enthalpy space uniformly* under some upper enthalpy cutoff (at which the system behavior approaches that of the ideal gas) and build a distribution of enthalpy values
3. Determine the median enthalpy (H_m) of the previously constructed enthalpy distribution
4. Sample uniformly* under the restriction $H < H_m$ and build a new distribution of enthalpy values.
5. Repeat steps 3 and 4 until some stopping criterion is met.

*Applying the volume selection criteria:

$$A(V_1 \rightarrow V_2) = \min[1, (V_2/V_1)^N]$$

From the Nested Sampling iterations the excess NPT partition function (Δ_{Ex}) at any temperature can then be determined as:

$$\Delta_{Ex} \approx \sum_n 2^{-n} e^{-\beta H_n}$$

Where H_n is the average enthalpy between H_m and H_{m-1} :

$$H_n = \frac{1}{2} (H_m + H_{m-1})$$

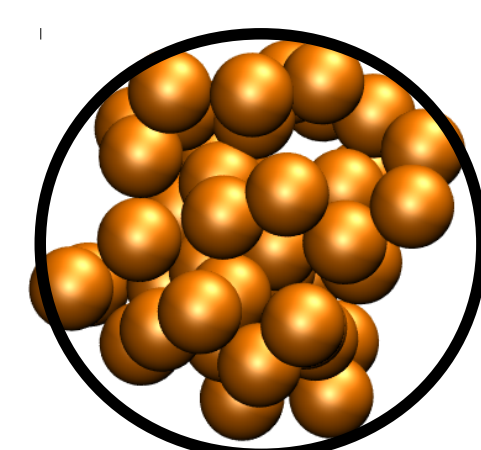
Recall that thermodynamic quantities can be derived from the partition function. For example:

$$H = -\frac{\partial \ln(\Delta_{NPT})}{\partial \beta} \quad C_p = \frac{\partial H}{\partial T} \quad S = k_B \ln(\Delta_{NPT}) + \frac{H}{T}$$

Enthalpy Heat Capacity Entropy

Model System

Isolated (N=55) Lennard-Jones (LJ) system with hard spherical boundary.

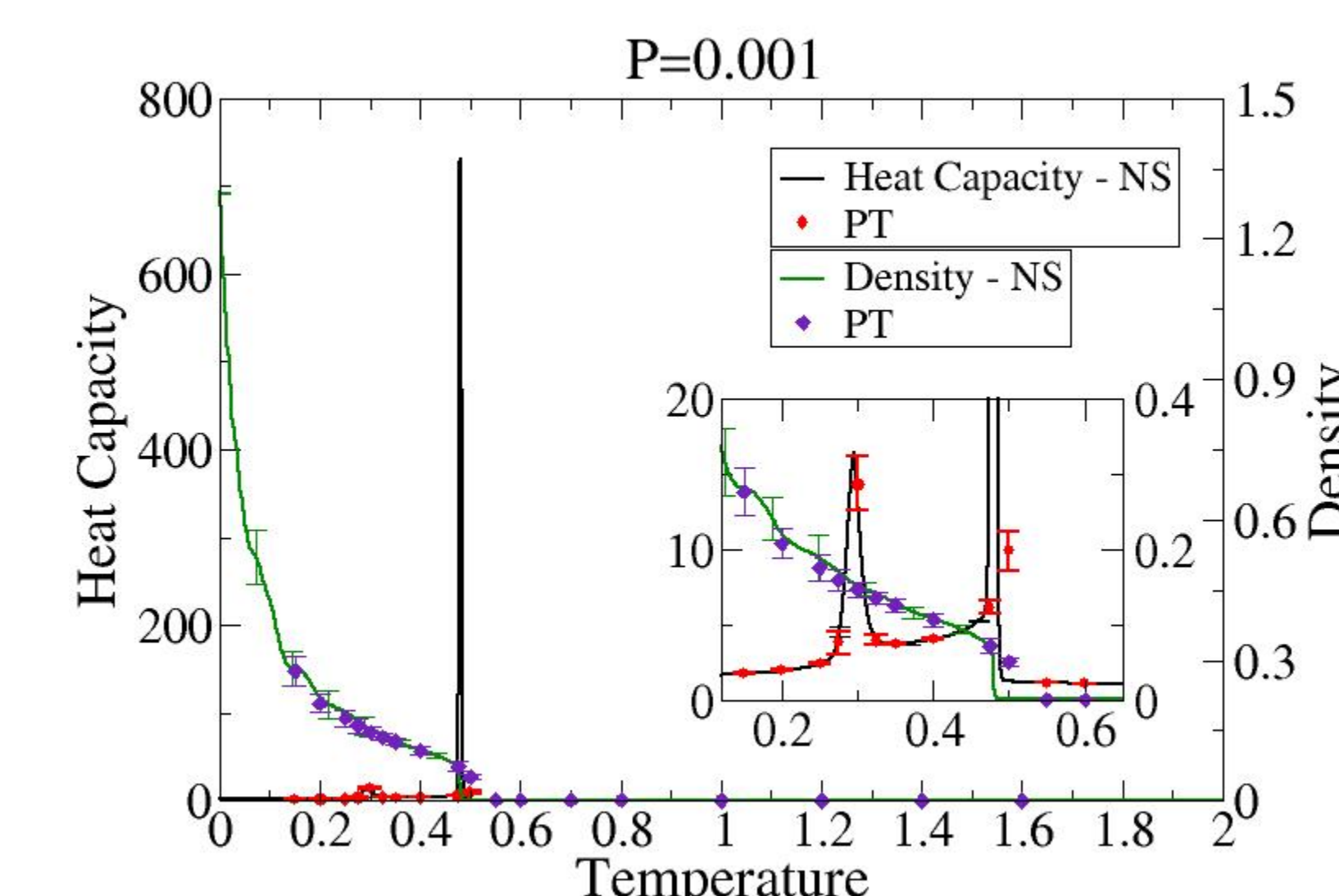
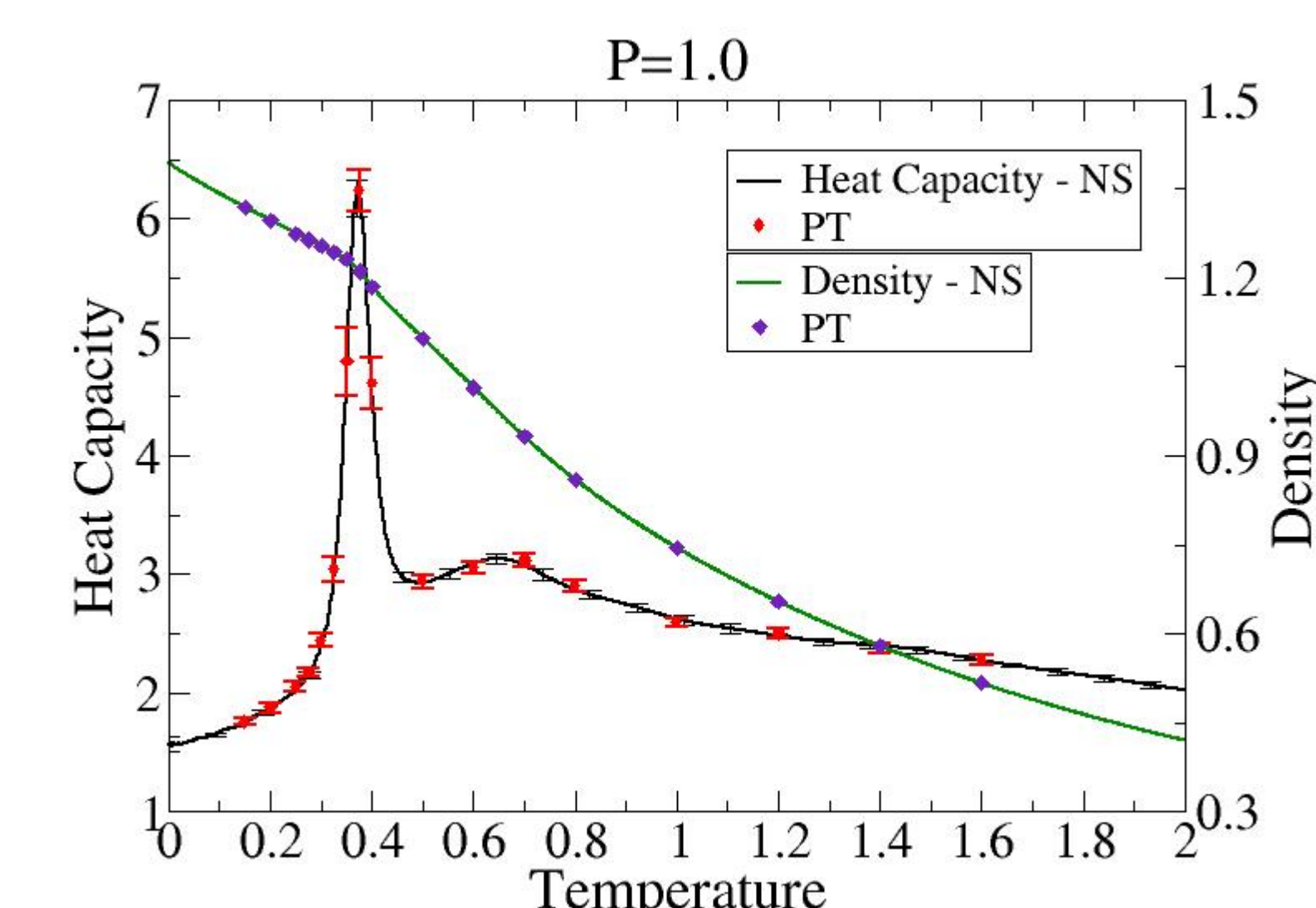


Pairwise LJ potential:
No cutoff is used.

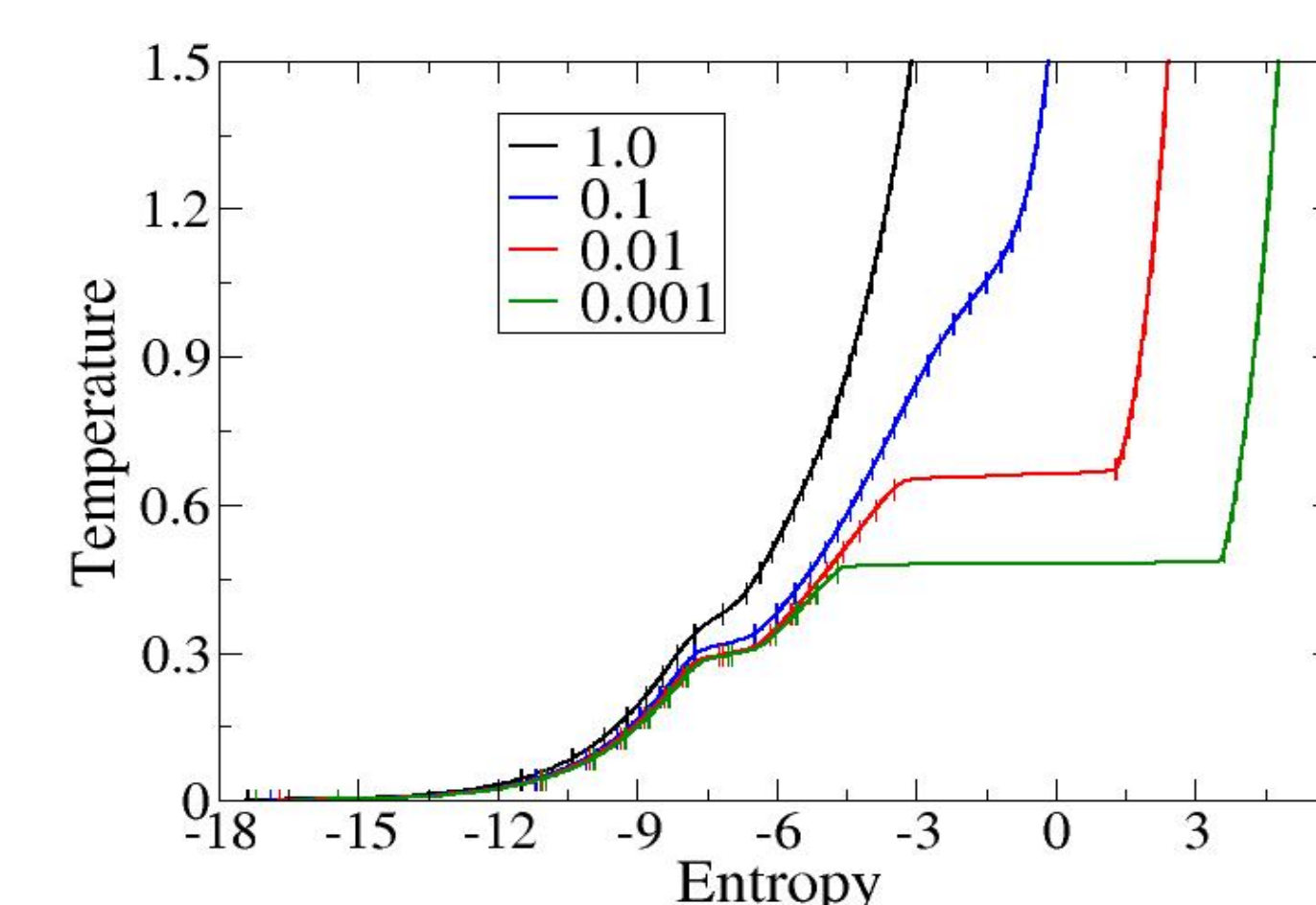
$$E_{ij} = 4\pi\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right]$$

Results

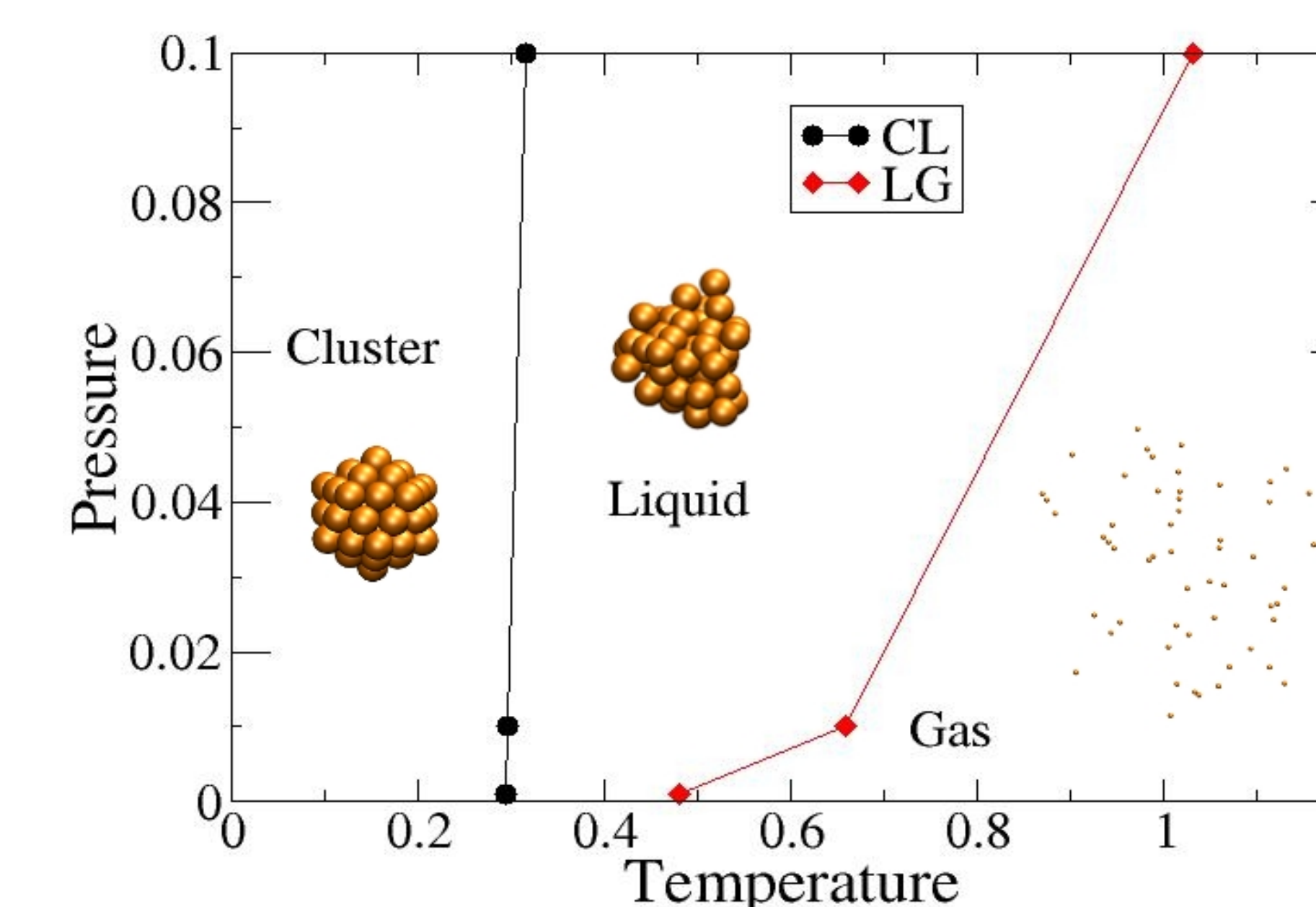
- Excess heat capacity and density versus temperature from Nested Sampling (NS) and Parallel Tempering (PT)



- Temperature vs. Shifted Excess Entropy at various pressures. (TS plot)



- Pressure-Temperature phase diagram. Includes pressures 0.001, 0.01, and 0.1



Conclusions

- A new computational method based on Nested Sampling to compute the NPT partition function and thermodynamic quantities has been successfully implemented
- Results are confirmed by comparison with Parallel Tempering
- The method is an excellent choice to simulate isobaric systems and generate TS plots and Pressure-Temperature phase diagrams

References

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