High Temperature Classical Thermodynamics

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Motivation

Many important applications in the fields of physics and chemistry that depend on understanding finite temperature classical thermodynamics. At high temperatures, the virial expansion (VE) acts as an approach to many-body thermodynamics that provides equations of state for various systems of interest. The focus of this project was to build on the existing automated algebra engine by Miller and Drut to explore a classical gas governed by the Coulomb interaction [1].

Formalism

The virial expansion organizes a many-body problem into a sum of N-body problems. Thermodynamic quantities are related to this expansion via the grand thermodynamic potential Ω as

$$-\beta\Omega = Q_1 \sum_{N=1}^{\infty} b_N z^n$$

where b_N are the virial coefficients. We focus on the calculation of the coefficient for an N = 2 particle system. This is done via the calculation of an integral in the form

$$\int dr_1 dr_2 f_{12}$$

where f_{12} is known as the Mayer *f*-function, defined by

$$f_{ij} = -1 + e^{-\beta v_{ij}}$$

where v_{ij} is the interaction potential between the particles.

Methods

The interaction potential of interest in this project is the Coulomb potential, given simply as

$$v_{12} = {}^{w}/_{r_{12}}$$

where r_{12} is the distance between the 2 particles, and *w* is a weight that varies between 0 and 1. Though this provides a fairly simple f_{12}, the integration is done by approximating

$$f_{12} \cong -e^{-b_1 {r_{12}}^2} + \sum_i A_i(-e^{-b_i {r_{12}}^2} + e^{-b_{i+1} {r_{12}}^2})$$

then exploiting the properties of this approximation such that the integral is calculated from the determinant of a symmetric positive definite matrix. We test whether a higher order approximation yields a better b_2 virial coefficient as well as the convergence of this approximation to the exact f_{12}.

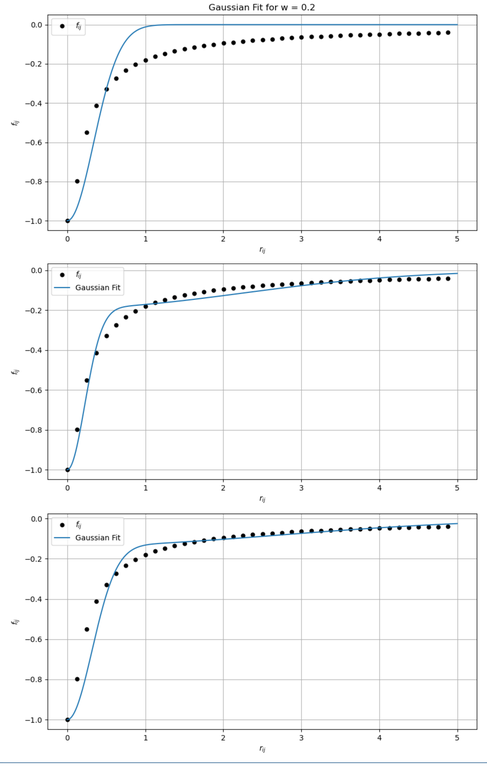

Fig. 1: Approximation of f_{12} with different numbers of terms for w = 0.2. From top to bottom: 3 terms, 5 terms, 7 terms. The accuracy of the approximation to the exact f_{12} increases with added terms.

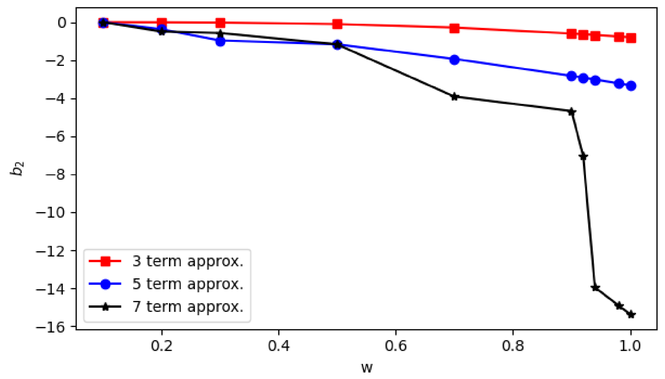

Fig. 2: Plot of calculated b_2 virial coefficient as a function of interaction weight *w*

Results and Outlook

The convergence of the f_{12} approximation behaves as expected: more terms yield a more accurate approximation (Fig. 1).

For the calculation of b_2, the added terms in the approximation seem to converge to a common value at low weights (Fig. 2). At higher weight values, however, the 7-term approximation diverges significantly.

Next steps of this project include a generalization to larger N via implementation of a symbolic method to multiply f_{ij}s, as well as an algorithm to determine whether a certain number of terms in the f_{ij} expansion provides a valid result.

References

[1]. Miller, A.M. and Drut, J.E. (2023) 'Calculating the classical virial expansion using automated algebra', *Physical Review E*, 108(6). doi:10.1103/physreve.108.065307.