RESOLVING THE INCONSISTENCY BETWEEN THE VIRIAL AND THERMODYNAMIC PRESSURE IN COULOMB SYSTEMS

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In this work, we compare approaches to calculate the pressure of Coulomb systems, specifically the thermodynamic and the virial pressure. The calculation of the thermodynamic pressure is based on the differentiation of the free energy over the volume to express the pressure through the position of the particles. Another commonly used method states that the pressure can be calculated via the virial pressure, expressed by the forces between system particles or an internal virial. [1]. This relationship comes from the virial theorem, which relates all forces acting on particles to the time-averaged kinetic energy of the system [2].

The method based on differentiation of the free energy leads to the well-known expression $PV = Nk_BT + E/3$ for the pressure of Coulomb systems P [3] for a given volume V (E is the potential energy, N is the number of particles). For the Coulomb potential, the virial and thermodynamic pressures coincide. However, if we calculate the pressure using the Ewald potential or its angular-averaged version [4], we obtain a quantity that shows no N-convergence.

We demonstrate that the problem of inconsistency between these two pressures arises from the explicit dependence of the potential energy on the volume of the system (i.e. on the length of the computational cell) [5] in the case of the Ewald technique. We show that if the potential energy is a homogeneous function of the particle coordinates and the computational cell length (which is fulfilled for the Ewald potential), then the internal virial and hence the virial pressure are expressed via the potential energy of the system, thus maintaining the well-known virial theorem for homogeneous potentials [2].

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