Anharmonic effects in molecular crystals using quasiparticle theory

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The development of novel molecular materials and new drugs often requires an understanding of the landscape of the observable crystal structures for a given molecule. The aim of crystal structure prediction (CSP) is the computational prediction of accurate and reliable molecular crystal landscapes. An accurate calculation of the vibrational free energy contributions is essential for the prediction of the energy landscape. At the density functional theory (DFT) level, finite temperature thermodynamic properties are accessible through ab initio molecular dynamics (AIMD) or the quasi-harmonic approximation (QHA). AIMD simulations provide accurate results, but its high computational cost (in combination with DFT) limits its applicability. QHA is computationally cheaper but its main drawback is the incomplete consideration of the anharmonicity in the vibrational energy, which may be particularly relevant for molecular crystals.

In this work we evaluate the performance of the recently implemented quasiparticle approximation (QP) [1], proposed by Allen, which allows the calculation of thermodynamic properties including anharmonicity at an affordable computational cost. In the QP approach, nth order force constants are used to derive volume- and temperature-dependent entropies, which are fitted with a Debye-like model to derive the remaining thermodynamic properties. Three model systems with featuring different intermolecular interactions (urea, anthracene, ethylcarbamate) are examined, and the impact of anharmonic corrections on the calculated thermodynamic properties is evaluated. The influence of the exchange-correlation functional on thermodynamic properties is also examined.

[1] Blancas, E. J., Lobato, A., Izquierdo-Ruiz, F., Márquez, A. M., Recio, J. M., Nath, P., Plata, J. J., and Otero-de-la-Roza, A. (2024) *npj Comput. Mater.*, **10**, 267