

First-principles thermodynamics of energetic materials

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FIRST-PRINCIPLES THERMODYNAMICS OF ENERGETIC MATERIALS

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Abstract. Using density functional theory with empirical van der Waals corrections, cold pressure curves were calculated and combined with the quasi-harmonic approximation to study thermodynamical properties of several energetic molecular solids. Vibration spectra at each compression were calculated and used for including temperature and zero-point energy contributions to the free energy. Equilibrium properties at temperatures of experiments, as well as hydrostatic equations of state, specific heat capacities, and coefficients of thermal expansion, were obtained and compared to experiment.

Keywords: energetic materials, equations of state, density functional theory, van der Waals, thermal properties

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INTRODUCTION

To perform meso-scale and continuum-level simulations of detonating energetic materials (EMs), accurate mechanical and thermal properties are required to provide meaningful results on explosive performance, as well as materials response to a variety of conditions [1]. Unfortunately, experiment falls short of providing these properties over a wide range of pressures and temperatures, and is hindered by inaccuracies from shear introduced by the compressive media used in diamond anvil cells [2]. As such, theoretical avenues for the acquisition of key input parameters for large-scale modeling of EMs have been a major thrust for the EM modeling community.

Initial efforts focused on calculating equations of state (EOSs) and thermal properties using pure density functional theory (DFT) methods; however, DFT with generalized gradient approximation (GGA) greatly over-predicted equilibrium volumes

by an average of 10% compared to experiment due to inadequate description of dispersive van der Waals (vdW) interactions [3,4]. More recently, attempts to economically incorporate vdW into DFT (DFT+vdW) led to various treatments using pair-wise C_6/r^{-6} potentials that are simply added to DFT at large distances [5,6]. While these approaches have been shown to vastly improve the prediction of equilibrium volumes in EMs, they systematically under-predict these volumes by about 3% [7]. Fortunately, this under-prediction was shown to be due to the exclusion of thermal and zero-point energy (ZPE) effects on the crystalline environment [8]. By including vdW, thermal, and ZPE effects into DFT (DFT+vdW+T), equilibrium volumes were predicted within 1% of those obtained by experiment, and very accurate EOSs were obtained [8].

In addition to obtaining mechanical properties of EMs by DFT+vdW+T, thermal properties are also of substantial interest. Therefore, the goal of

this work is to calculate thermal properties, such as heat capacities and coefficients of thermal expansion (CTEs), for EMs using the DFT+vdW+T approach, and compare these predicted properties to those of experiments.

COMPUTATIONAL DETAILS

The DFT+vdW+T approach used in this work is based on standard DFT with the Perdew-Burke-Ernzerhof exchange-correlation functional and the empirical vdW treatment of Neumann and Perrin [6]. The vdW method employed uses $C_6 r^{-6}$ pairwise potentials multiplied by a damping function that prevents divergence of $1/r^6$ at small r .

$$d_{AB}(r) = \left(1 - \exp \left[- \left(\frac{r}{R_{AB}} \right)^{\frac{3}{n}} \right] \right)^{2n} \quad (1)$$

The damping function, d_{AB} in (1), contains two parameters that were fit to experimental data for cold ($T < 50\text{K}$) molecular crystals: the form factor n , which alters the shape of the damping function; and the crossover distance R_{AB} , which defines the short-distance cutoff for vdW interactions.

The DFT+vdW approach was used to calculate hydrostatically compressed and expanded cold-pressure structures for which the atoms were relaxed to a maximum force of 0.03 eV/\AA . For each compression/expansion, the dynamical matrix is calculated by finite displacement with a step size of $\pm 0.05 \text{ \AA}$. Diagonalizing these matrices give vibration spectra under the quasi-harmonic approximation, which can then be used to calculate free energies and thus equilibrium volumes for the EMs studied at various temperatures; see Ref. [8]. Additionally, the vibration spectra were used to calculate heat capacities and CTEs up to melt temperatures for comparison to experiment.

RESULTS AND DISCUSSION

As seen in Figure 1, EOSs were calculated for both nitromethane (NM) and PETN-I using pure DFT, DFT+vdW, and DFT+vdW+T. Evidenced by their relation to experiment (triangles) pure DFT over-predicts, while DFT+vdW under-predicts the EOSs. Only when temperature and ZPE effects are included is good agreement with experiment obtained. For instance, the unit cell volume for

PETN-I determined by experiment [9] at 300 K is 589.5 \AA^3 , and is predicted to be 590.7 \AA^3 by DFT+vdW+T. Likewise, NM at 4.2 K was determined [10] to be 275.3 \AA^3 , but was also predicted to be 275.3 \AA^3 by DFT+vdW+T. Additionally, the resulting bulk moduli for NM and PETN-I are 7.9 and 12.8 GPa respectively, which compares favorably to the values 8.3 and 12.3 GPa obtained by experiment [11,12]. This demonstrates the ability of DFT+vdW+T to reasonably predict bulk moduli.

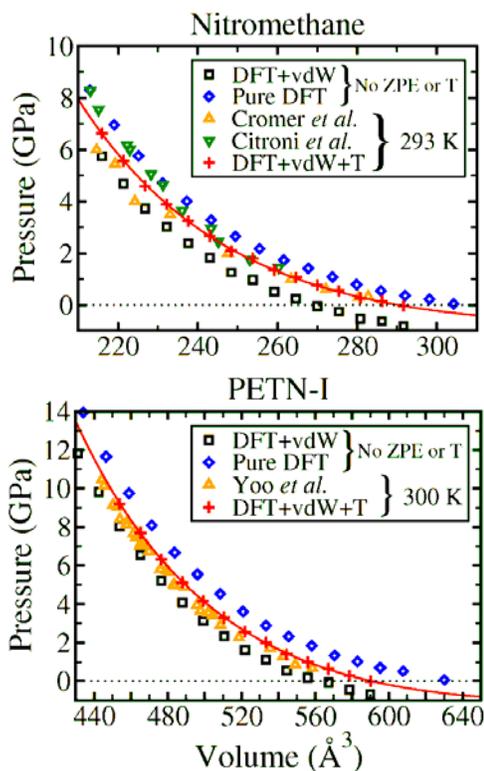


Figure 1. EOSs for NM and PETN-I showing agreement between experimental data (triangles) and data calculated using DFT+vdW+T (crosses). Solid line is B-M fit for calculated data.

The predictive value of the DFT+vdW+T approach for mechanical properties of EMs suggests its potential for predicting thermal properties such as heat capacities or CTEs over a wide range of pressures and temperatures. In fact, as seen in Figure 2 (top and middle), fairly good agreement can be seen in the cases of NM and PETN-I at ambient pressure; however, the values

obtained from calculation diverge from those obtained from experiment approaching the melt temperature. Additionally, the bottom plot in Figure 2 shows the rather poor agreement of the calculated CTE as compared to that obtained by experiment for PETN; where other EMs showed even worse agreement, and thus are not reported here for compactness. Clearly the small discrepancies in heat capacities, and the large discrepancies in CTEs, result from inaccuracies in the vibration spectrum, particularly the low frequency modes, to which heat capacity and CTE are most sensitive, and free energy is least sensitive. To sufficiently sample intermolecular modes, a 1x1x2 cell was used for PETN-I such that the minimum dimension of the most compressed structure was not less than 8.5 Å. Likewise, a 2x2x1 cell was used for NM.

To rule out both inaccuracies in forces, and sampling of the dynamical matrix beyond the harmonic limit, the force convergence criteria was lowered to 0.01 eV/Å, while the finite displacement step size was lowered to ± 0.02 Å. These changes resulted in slight improvement to heat capacity, and significant improvement to CTE for PETN-I as seen in Figure 2 (middle and bottom). Nonetheless, the goal of achieving excellent quantitative agreement with experiment had not been achieved. Additionally, it was found that despite the lack of a polymorphic change, the calculated low-frequency, intermolecular modes exhibited non-monotonic behavior with volume, suggesting that the problem may be due to errors introduced by the vdW damping function at intermolecular distances. As a final note, the error for the calculated equilibrium volume of PETN-I increased from +0.2% to +1.2%, which can be explained by the fact that the damping function was fit to lattice parameters of low-temperature crystals with ZPE effects still included.

To get a sense of how the vdW damping function might affect the calculation of the dynamical matrix, the vdW interaction for two N atoms was plotted along with its first and second derivatives with respect to distance; see Figure 3. The narrow peak in the first derivative, and subsequently the resulting rapid change in the second derivative, can greatly affect interactions within the dynamical matrix for atoms separated by distances close to the crossover distance when both

positive and negative displacements are made for the same atom. Further, the bulk of intermolecular interactions for EMs occur within ± 2 Å of the crossover distance, undoubtedly leading to poor description of intermolecular modes with respect to volume.

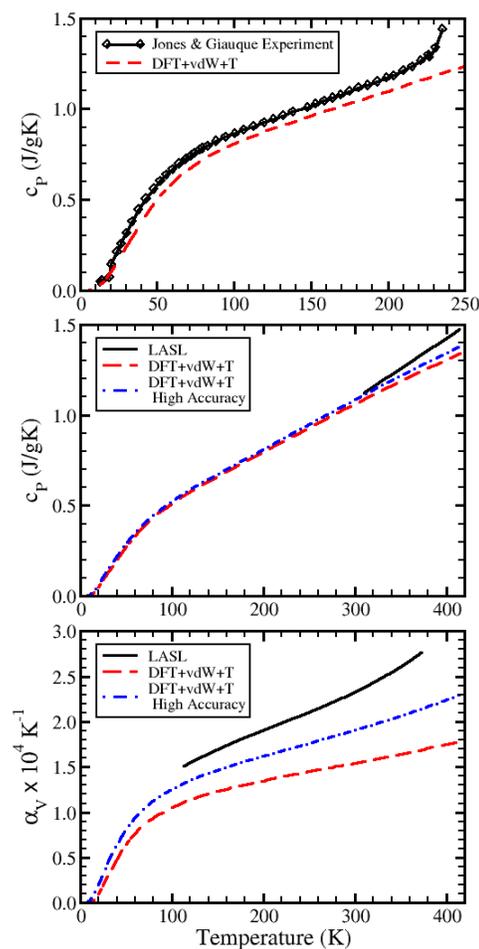


Figure 2. Specific heat capacity for NM (top) and PETN-I (middle), as well as CTE for PETN-I (bottom). For PETN-I, the high accuracy curves correspond to lowered force convergence criteria and smaller step size for finite displacement.

CONCLUSIONS

In summary, DFT+vdW+T predicts well the EOSs of EMs over ranges available from experiment, but does only moderately well for heat capacities and poorly for CTEs – both being

sensitive to low frequency modes. The discrepancies seem to be due to inaccuracies in low-frequency, intermolecular modes brought on by the non-monotonic behavior of the second derivative of the empirical vdW interaction. This is a direct effect of the damping function form used to shut-off vdW interactions at small distances. Further refinement to the damping function form, as well as fits to crystallographic data extrapolated to cold pressure values to redundancy in the treatment of ZPE effects, should greatly improve accuracy in the prediction of thermal properties of EMs, and further refine accuracy for EOSs.

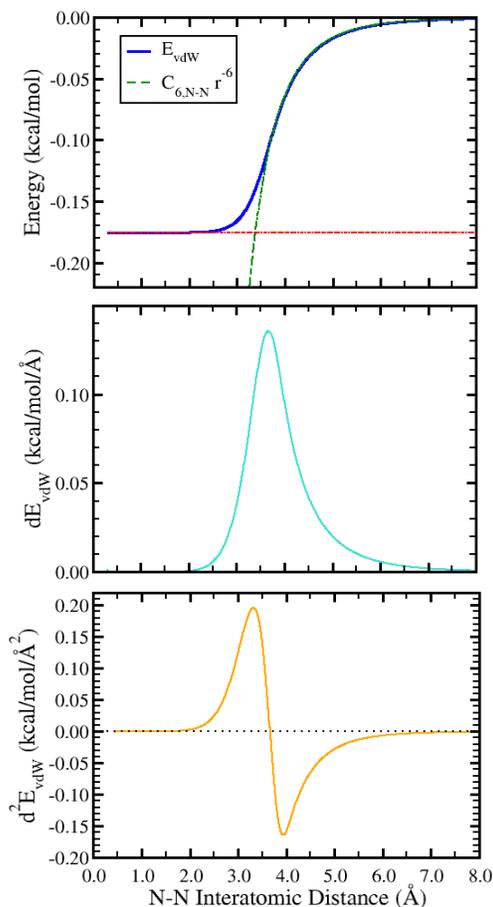


Figure 3. Calculated vdW binding energy curve (top) for prototypical two nitrogen atom system with first spatial derivative (middle) and second spatial derivative (bottom) demonstrating inaccuracies introduced near the crossover distance ($R_{N-N} = 3.384 \text{ \AA}$).

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