Phase stability of the argon crystal: first-principles study based on random phase approximation plus renormalized single excitation corrections

Sixian Yang\textsuperscript{1} and Xinguo Ren\textsuperscript{2,3,}\textsuperscript{*}

\textsuperscript{1} Key Laboratory of Quantum Information, University of Science and Technology of China, Hefei 230026, People’s Republic of China
\textsuperscript{2} Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People’s Republic of China
\textsuperscript{3} Songshan Lake Materials Laboratory, Dongguan 523808, Guangdong, People’s Republic of China

\textsuperscript{*} Author to whom any correspondence should be addressed. E-mail: renxg@iphy.ac.cn

Keywords: density functional theory, random phase approximation, rare gas crystal, phase transition, non-local electron correlation

Abstract

The energy differences between the face-centered cubic (fcc) and hexagonal closed packed (hcp) structures of the argon (Ar) crystal are studied using the first-principles electronic-structure approach at the level of random phase approximation (RPA) plus renormalized single excitation (rSE) correction. By treating both structures at equal footing (i.e., employing the same computational supercell and \( k \) grid sampling), our RPA\textsuperscript{+}rSE calculations show that, at zero temperature, the fcc structure is lower in energy than the hcp structure over a wide pressure range. The influence of zero-point energy (ZPE) is also studied and it is found that ZPE only plays a secondary role in determining the relative stability of the two structures, whereas the electron correlation effect dominates. We further examine the equation of states in the high pressure regime, and our RPA\textsuperscript{+}rSE results, complemented with phonon contributions, show excellent agreement with available experimental data. Finally, by computing the Gibbs free energies for both the fcc and hcp at different temperatures, we are able to generate a \( T-P \) phase diagram for the Ar crystal, disclosing the pressure–temperature range for each phase. Our calculations show that the fcc phase has a slightly larger entropy and volume than hcp phase at the temperature and pressure condition.

1. Introduction

An essential goal of computational physical science is to reliably predict the relevant polymorphs and their relative stability, and consequently the thermodynamic behavior of a substance, with only knowledge of its chemical composition. This challenge largely persists even today after it was noted over 30 years ago [1]. Nevertheless, considerable progress has been made toward this goal, thanks to the development of various structure prediction algorithms [2–6] as well as the continuing methodology and accuracy advances of first-principles calculations [7–12]. Nowadays, it is not uncommon for the mainstream crystal structure prediction (CSP) methods to predict the relevant known and unknown polymorphic forms of a material, as well as their energy separations, starting with a pre-given chemical composition. However, the output of such predictions, in particular the energy ranking of different polymorphs will necessarily depend on the underlying electronic structure methods for computing the potential energy surface. For instance, most CSP algorithms can predict the existence of diamond and graphene allotropes for carbon, but cannot tell graphene is thermodynamically more stable at ambient conditions, if conventional local/semilocal density functional approximations (DFAs) are employed as the electronic structure solver. Similar issues occurs if
One quest for whether the face-centered cubic (fcc) or hexagonal close packed (hcp) crystal structure is preferred for rare gas crystals under ambient pressure [13, 14]. Thus, in the long-term endeavor aiming at quantitatively and faithfully predict the thermodynamical behavior of real materials without invoking empirical inputs, further improving the accuracy and reliability of the underlying electronic structure methods that can be conveniently used together with the CSP algorithms is a must.

In fact, the above-noted phase stability of rare-gas crystals has posed a significant challenge to first principles electronic structure methods. In particular, it is theoretically highly nontrivial to describe the delicate energy differences between the fcc and hcp phases at zero temperature, for which a sub-meV accuracy is mandatory. Without a solid base at 0 K, it is then highly unlikely that one can convincingly explain why rare gas atoms prefer to crystallize in the fcc phase instead of the hcp phase under ambient pressures, let alone the entire phase diagram of the rare-gas systems under varying thermodynamic conditions. Within the realm of first principles electronic structure theories, conventional local and semilocal DFAs [15, 16] are unable to reliably describe the cohesive properties of rare-gas systems due to their inadequate treatment of long-range van der Waals (vdW) interactions. Complementing semi-local functionals with semiempirical vdW corrections [17–20] or non-local vdW density functionals [21, 22] can significantly improve their usefulness in describing vdW-bonded systems, but it is questionable whether these pragmatic vdW-inclusive schemes can provide the needed (sub-meV) accuracy in order to describe the phase stability of rare-gas crystals. Beyond these approximations one may either go to the fifth-rung functionals [23] (e.g., the random phase approximation (RPA) [24–28] and beyond [29, 30]) within the realm of the density functional theory (DFT) where non-local electron correlation effects are seamlessly incorporated, or simply go to wave-function based approaches, like the second-order Møller–Plesset perturbation theory (MP2) [31] and the coupled cluster (CC) theory [32]. However, MP2, which contains only two-body (here ‘body’ means atom) correlations, is considered not sufficiently accurate to describe the cohesive properties of rare-gas crystals [33–35].

In the connection, the CC theory truncated at the level of single, double, and perturbative triple excitations (CCSD(T)) [36] (known as ‘gold standard’ in computational chemistry) is of great interest and has been applied to study the cohesive properties of rare-gas systems [33–35, 37–42]. However, in these studies, instead of directly applying CCSD(T) to treat infinite periodic rare-gas crystals, one utilizes the method only to generate the short-range part of the potential energy landscapes of trimers and tetramers. The entire cohesive energies are obtained by summing up two-body, three-body, and four-body contributions, with each of them being calculated by summing over sufficiently large atomic clusters in real space. The interactions between atomic pairs, as well as the long-range part of the interactions within trimers and tetramers are being described by empirical model potentials. Thus this is a rather sophisticated approach that combines many ingredients into a framework, and necessarily depends on many parameters. Despite the remarkable accuracy this approach delivers and its successful explanation of the preference to the fcc phase of rare-gas crystals [40], it is rather tedious to use for non-experts and barely suitable for routine applications, in particular in the context of high-throughput computations.

In this work, we present a detailed study of the performance of RPA and beyond for computing the cohesive energies of the Ar crystal, with special emphasis on the energy differences between the fcc and hcp phases. Here RPA refers to a theoretical approach for computing the ground-state total energy of many-electron systems, in a way that the exchange energy is evaluated exactly and the electron correlation energy is treated at the direct RPA level. The exchange-correlation (XC) energy of the RPA method can be viewed as an orbital-dependent energy functional derived within the framework of adiabatic-connection fluctuation–dissipation theorem of DFT [25, 26, 43], but it is also intimately connected to the CC theory [44]. One particularly appealing aspect of RPA is that it provides a balanced description of all bonding characteristics, whereby the vdW interactions are incorporated seamlessly. Early benchmark studies indicated that RPA (and beyond) is capable of describing delicate energy differences [28]. This is corroborated by more recent studies that revealed that RPA yields the correct energy ranking of different polymorphs of several types of materials, including carbon allotropes [45], FeS2 [46], BN [47], as well as a few others [48].

Despite its success, the standard RPA scheme shows an overall tendency of underestimating the binding energies of molecules and solids [49, 50], and this underestimation can be largely alleviated by adding a correction term arising from single excitations [51]. In particular, the renormalized single excitation (rSE) correction has been shown to appreciably improve the accuracy of the standard RPA for describing the binding strengths of molecules and solids [30, 52, 53]. In this work, we apply the RPA+rSE method [30] to study the energy difference between the fcc and hcp structures of the Ar crystal. Here, instead of resorting to a tedious cluster-based approach [37–42], we directly treat the crystal as a periodic system in terms of $k$ point sampling. We find that, in order to capture the delicate energy differences between the fcc and hcp
structures, it is important to treat the two structures at an equal footing, i.e., setting up a computational cell that is the same for the fcc and hcp crystal structures and performing calculations with the same \textbf{k} point setting. Test calculations show that using their primitive unit cells of these two structures (and hence different \textbf{k} point setting) will not provide sufficient numerical precision. With the above-noted computational strategy, and by carefully converging all the computational parameters, we found that the RPA+rSE cohesive energy for the fcc phase is lower by around 3.6 $\mu$Ha ($\sim$0.1 meV) than that of the hcp phase at zero temperature and ambient pressure. The zero-point energy (ZPE), which was previously suggested to be vital for stabilizing the fcc phase [38–40], is found to only play a secondary role. Furthermore, by including the contributions of phonon energies, we calculate the Helmholtz free energy and derive the pressure–volume ($P$–$V$) curves at room temperatures. Our results are in excellent agreement with available experimental data in the high-pressure regime, which was previously considered to be a challenging problem for the Ar crystal [42]. Finally, by computing the Gibbs free energy for both phases, we are able to determine the phase boundary of the fcc and hcp phases in the temperature–pressure ($T$–$P$) phase diagrams. The behavior of the phase boundary line can be understood from the perspective that the fcc phase has a slightly large entropy and volume than the hcp phase at the same temperature and pressure conditions.

Our investigation suggests that the combination of advanced electronic structure calculations at the level of RPA and beyond with reliable estimations of phonon energies is a powerful approach to study the thermodynamic properties of condensed matter systems. Since the implementation of such an approach has been available in several mainstream computer codes and the barrier of employing such an approach for routine application is not high, we expect this approach will become highly useful for tackling challenging problem when high accuracy is required.

2. Methodology and computational details

2.1. The computation of RPA+rSE total energy

The ground-state total energy in this work is calculated using the RPA+rSE method, whereby the total energy is given by

\[ E_{\text{RPA+rSE}} = E_{\text{DFA}} - E_{\text{xcorr}} + E_{\text{xc}} + E_{\text{RPA}} + E_{\text{rSE}}, \]

whereby \( E_{\text{DFA}} \) is the total energy of a conventional DFA and \( E_{\text{xcorr}} \) is its XC component. Furthermore, \( E_{\text{xc}} \), \( E_{\text{RPA}} \), and \( E_{\text{rSE}} \) are respectively the exact-exchange energy, the RPA correlation energy, and the rSE correlation energy, evaluated using the DFA orbitals and orbital energies. We utilize the existing RPA+rSE implementation available in the all-electron full-potential code package FHI-aims [29, 54], based on the numerical atom-centered orbital (NAO) basis set framework. Comprehensive reviews of the RPA method for many-electron ground-state energy calculations exist in the literature [27, 28, 55] and its rSE correction has been discussed in reference [30]. In the same work [30], the performance of RPA+rSE for molecular systems has been thoroughly benchmarked, where it was shown that RPA+rSE performs rather well (with only 0.2 kcal/mol mean absolute error with reference to CCSD(T) results) for weak interactions (including hydrogen bonding, dispersion bonding, and mixed bonding characters), as exemplified by the S66 test set [56]. Recently, the excellent performance of RPA+rSE for describing the energy hierarchy of different isomers of water clusters has been demonstrated in a study reported in reference [57]. In general, the RPA+rSE method is considered to be more reliable than the vdW-inclusive DFA schemes like PBE complemented with the Tkatchenko–Scheffler (TS) vdW correction (vdW(TS)) [19] and/or Grimme’s PBE-D3 [18] since the former is fully \textit{ab initio}, whereas vdW(TS) and D3 corrections are of semi-empirical nature. But this of source comes at the expense of a steep increase of the computational cost.

The numerical details and benchmark tests for NAO-based RPA (and rSE) implementation for finite systems (molecules and clusters) have been presented in references [29, 30, 58]. Recently, this implementation has recently been extended to periodic systems. While the details will be presented elsewhere, the basic numerical techniques of periodic RPA implementation within the NAO framework follow closely those of periodic GC$_6$W$_6$ implementation published recently [59]. Also, the reliability of our NAO-based periodic RPA implementation has been demonstrated by recently published benchmark-quality calculations for a set of semiconductors [60].

The valence correlation-consistent (VCC) NAO basis sets [61] are used in our calculations. Such basis sets allow one to extrapolate the calculated RPA+rSE results to the complete basis set (CBS) limit, if the following asymptotic behavior is assumed [62]

\[ E(n) = E(\infty) - C/n^3. \]
In equation (2), \( n \) is the cardinal number of the NAO-VCC-\( nZ \) basis sets \([61]\), and \( C \) is a fitting parameter. Our CBS results for RPA+rSE are then obtained from a two-point extrapolation with \( n = 3, 4 \) \([60, 62]\)

\[
E(\infty) = \frac{E(3)3^3 - E(4)4^3}{3^3 - 4^3} \tag{3}
\]

and hence denoted as CBS(3, 4). The semi-local or hybrid functionals utilize only occupied state information and the convergence with respect to the basis set is much less demanding. Hence, in the present work, the NAO-VCC-4Z basis set is used for these functionals. Figure S1 in the supplemental material (SM) (https://stacks.iop.org/NJP/24/033049/mmedia) demonstrates the basis set convergence behaviors of both RPA+rSE and PBE calculations.

As already mentioned in the introduction, to obtain reliable energy differences between the fcc and hcp structures, it is crucial to treat both structures on an equal footing. To this end, a computational supercell that is the same for two structures, and treating them completely on the same footing.

The computational cost of the RPA calculations scales as \( N_b^4 \) with respect to the number of basis functions \( N_b \). To reduce the computational load, the NAO-VCC-4Z RPA+rSE results for the six-atom computational cell at a given volume \( V \) (denoted as \( E_{4Z}(V) \)) are obtained from the NAO-VCC-3Z results \( (E_{3Z}(V)) \) upon adding a correction term that is obtained from calculations based on the primitive unit cells, \( E_{4Z}(V) = E_{3Z}(V) + E_{\text{corr}}(V) \).

Here,

\[
E_{\text{corr}}(V) = N_c \ast \left[ E_{4Z}^{\text{prim}}(V) - E_{3Z}^{\text{prim}}(V) \right], \tag{5}
\]

where \( E_{4Z}^{\text{prim}}(V) \) and \( E_{3Z}^{\text{prim}}(V) \) are respectively the NAO-VCC-4Z and NAO-VCC-3Z results for primitive unit cells, and \( N_c = 6 \) (3) for fcc (hcp) structures. In these calculations, \( 12 \times 12 \times 2, 12 \times 12 \times 12 \) \((12 \times 12 \times 6) \) \( k \) grids are used for the supercell and fcc (hcp) primitive cells, respectively. Test calculations show that such a basis correction scheme only introduces errors less than 0.1 \( \mu \)Ha for the energy differences between fcc and hcp structures, compared to direct NAO-VCC-4Z calculations for the supercell.

2.2. ZPE and free energy calculations

The Helmholtz free energy at a given volume \( V \) and temperature \( T \) invoked to determine the \( P-V \) curve presented in figure 3 is given as follows,

\[
F(V, T) = E^{\text{RPA+rSE}}(V) + \frac{1}{2} \sum_{q,j} \hbar \omega_q \delta_{V, q} + k_B T \sum_{q,j} \ln \left[ 2 \sinh \left( \frac{\hbar \omega_q \delta_{V, q}}{2k_B T} \right) \right], \tag{6}
\]

where \( E^{\text{RPA+rSE}}(V) \) is the RPA+rSE total energy at 0 K, and the second and third terms correspond to the contributions of ZPE and lattice vibrations at finite temperatures, respectively. In equation (6), \( \omega_q \delta_{V, q} \) are the phonon frequencies, which in the present work are calculated using the finite displacement method via the PHONOPY code \([63]\) interfaced with FHI-aims. The phonon spectra used to determine the ZPE and/or lattice vibration contributions presented in this work (cf figures 2–4 in section 3) are evaluated using the PBE functional with a \( 2 \times 2 \times 2 \) supercell (in units of the \( 1 \times 1 \times 6 \) computational cell, 48 atoms in total).

In the phonon calculations, \( 12 \times 12 \times 6 \) \( k \) grid and a displacement of 0.002 \( \AA \) (for the finite displacement method) are adopted. The influences of different functionals on the phonon spectra, and hence on the final ZPE and the energy differences between fcc and hcp structures, as well as on phonon contributions to the Helmholtz free energy and the derived \( P-V \) curves are illustrated in figures S3–S5 of the SM.

The Gibbs free energy used to determine the \( T-P \) phase diagram reported in figure 3 is given by

\[
G(T, P) = F(V, T) + PV. \tag{7}
\]
The Gibbs free energies are calculated separately for the fcc and hcp phases, and the phase boundary separating the two phases are determined by equating $G_{\text{fcc}}(T, P)$ and $G_{\text{hcp}}(T, P)$ at several different temperatures.

3. Results and discussions

3.1. Cohesive energy curves for the Ar crystal

We start by first looking at the performance of RPA+$rSE$ for describing the cohesive property of the Ar crystal. In figure 1 we present the cohesive energies as a function of the lattice constant for the fcc Ar crystal, as determined by various functionals, including RPA@PBE and (RPA+$rSE$)@PBE. Here ‘@PBE’ signifies that the calculations are done on top of the reference wavefunctions generated by a preceding KS calculation based on the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [16]. For comparison, results obtained using other functionals, including local-density approximation (LDA), GGA–PBE itself, the global hybrid functional PBE0 [64], the Heyd–Scuseria–Ernzerhof (HSE) screened hybrid functional [9], as well as PBE complemented with vdW(TS) [19] and with the more sophisticated many-body dispersion (MBD) [20], are also presented. In addition, the experimental equilibrium lattice constant and cohesive energy are indicated by dashed lines in figure 1. As discussed in section 2, all calculations are done using the FHI-aims code package [29, 54], based on an all-electron, numeric atom-centered orbital (NAO) basis set framework. The correlation-consistent NAO-VCC-nZ basis sets [61] are used in the calculations. Since correlated methods like RPA and beyond have different basis set convergence behavior compared to the conventional functionals, the presented RPA and RPA+$rSE$ results are those extrapolated to the CBS limit, whereas the results of other functionals are obtained with NAO-VCC-4Z basis set. The basis convergence behaviors of PBE and RPA@PBE calculations using the NAO-VCC-nZ basis sets are illustrated in figure S1 of SM. Figure 1 clearly shows that a quantitatively accurate description of the cohesive properties of the Ar crystal is highly challenging for first-principles approaches. While LDA displays a pronounced artificial overbinding, GGA-PBE shows the opposite behavior. Going from PBE to the hybrid functionals does not improve the situation, due to the fact that long-range vdW interactions are missing in both types of these functionals. Complementing the PBE functional with semi-empirical vdW corrections significantly improves the cohesive energies, as shown by PBE+vdW(TS) and PBE+MBD curves in figure 1, but the equilibrium lattice constant is still appreciably underestimated. In case of RPA-based approaches, RPA@PBE performs significantly better than LDA, GGA, and hybrid functionals, and the obtained equilibrium lattice constant (5.365 Å) is in excellent agreement with the experimental value (5.311 Å). However, similar to the Ar dimer (Ar$_2$) case [51], RPA@PBE underestimates the cohesive energies. Finally, when adding the $rSE$ correction, this underbinding is largely alleviated, and the (RPA+$rSE$)@PBE cohesive energy curve shows a rather satisfactory agreement with the experimental data, despite that a slight underestimation of the cohesive energy is still noticeable. It should be noted that RPA [65] and RPA+$rSE$ [53] have been previously applied to the fcc phase of the Ar crystal, using an independent implementation based on the projector augmented wave (PAW) method and plane-wave basis set [66]. In their paper [53], an even better agreement of the RPA+$rSE$ cohesive energy with the experimental result was reported. We expect such a slight difference arising from the different numerical implementations does not affect the discussions below.

3.2. Energy differences between fcc and hcp structures

Encouraged by the excellent performance of RPA+$rSE$ for describing the cohesive properties of the Ar crystal, we set out to examine the energy difference between the fcc and hcp structures of Ar using this approach. As discussed in section 2.1, to treat fcc and hcp on an equal footing, we set up a $1 \times 1 \times 6$ supercell for both structures, whereby the $z$ axis is chosen along the [111] direction of the fcc structure and the $c$ direction of the hcp structure, respectively. This results in a supercell with $ABCABC$ stacking for the fcc structure and with $ABABAB$ stacking for the hcp structure. Then by utilizing the same setting for $k$-point mesh ($12 \times 12 \times 2$ in the present case), one achieves a numerical description of both structures on an equal footing. As a consequence, the target energy differences of the two structures are least prone to possible numerical errors arising from the under-convergence of computational parameters. The importance of such a computational setup is illustrated in figure S2 of the SM. In figure 2, we plot the energy differences of the cohesive energies of the fcc and hcp structures obtained by PBE, PBE+MBD, PBE+vdW(TS), and (RPA+$rSE$)@PBE as a function of the volume. It can be seen that, most strikingly, the (RPA+$rSE$)@PBE yields a lower energy for the fcc phase than the hcp phase over a wide volume range. The energy preference to the fcc phase is approximately $3.5 \mu\text{Ha}$ at the ambient pressure, and reaches its maximum ($\sim 10 \mu\text{Ha}$) at a compressed volume of approximately $22 \text{Å}^3$ per atom. The energy difference is
Figure 1. Cohesive energies of the fcc Ar crystal determined by different functionals. All calculations are done using the FHI-aims code package [29, 54] and NAO-VCC-nZ basis sets [61]. The RPA and RPA+rSE results are obtained by extrapolating the NAO-VCC-3Z and 4Z results to the complete basis set (CBS) limit, and all other results are obtained using the NAO-VCC-4Z basis set. A primitive unit cell and $10 \times 10 \times 10$ k grid sampling are used in all calculations. ZPE contribution is not included here. Experimental values are taken from reference [67].

In addition to the electronic energies, it has been pointed out in the past that the ZPE plays an essential role in stabilizing the fcc phase over the hcp phase [38–40]. To check this point, we further add the differences of the ZPE contributions of the two phases to the RPA+rSE results, and plot the resultant RPA+rSE+ZPE results in figure 2 (blue curve). It can be seen that the ZPE contribution indeed favors the fcc phase, shifting the entire $E_{\text{fcc}} - E_{\text{hcp}}$ curve further down. However, its effect is much smaller in magnitude compared to the electron correlation effect described by RPA+rSE. It should be noted that in figure 2 the ZPE contributions are calculated using the PBE functional within the harmonic approximation. In principle, it would be ideal if the phonon frequencies were evaluated by the RPA+rSE approach. Unfortunately, at present our implementation does not yet allow one to compute the phonon spectra according to the RPA+rSE potential energy surface, and evaluate the ZPE contributions at the RPA+rSE level. However, as shown in figure S3 of the SM, we have checked the ZPEs using LDA, PBE and PBE+MBD functionals (among which the cohesive behavior of RPA+rSE sits in between), and confirmed that the ZPE contribution to the energy difference does not change appreciably with respect to the underlying functionals. We thus expect that the scenario illustrated in figure 2 does not change if RPA+rSE were used to evaluate the ZPEs. The anharmonic correction to the ZPE has also been considered in the literature [40], but its effect is rather small and neglected here.

3.3. The $P$–$V$ curve in the high-pressure regime

Besides the mystery regarding the preferred crystal structure at ambient pressure, the rare-gas systems in the high-pressure regime also exhibit fascinating phenomena. These include the pressure-induced structural
Figure 2. Energy differences between the fcc and hcp structures of the Ar crystal at zero temperature as a function of the volume (per atom). Presented results are calculated using PBE, PBE+MBD, PBE+vdW(TS), (RPA+rSE)@PBE approaches. Also shown are the (RPA+rSE)@PBE cohesive energy complemented with ZPE at the PBE level, denoted as ‘RPA+rSE+ZPE’. Results from RPA+rSE and ZPE@PBE are extrapolated to CBS(3, 4), while those from other functionals are obtained using NAO-VCC-4Z basis set. The presented curves are obtained by subtracting the corresponding cohesive energy curves of the fcc and hcp structures, which themselves are obtained by a second-order Birch–Murnaghan fitting of the original computed data.

phase transition from fcc to hcp (or to other structures at even higher pressures), the change of electronic structure, e.g., the narrowing of the band gap and/or the change of conductance [68], as well as the rearrangement of electronic states [69], etc. Even superconductivity has been predicted to exist at very high pressures [70]. Considerable efforts have been devoted to understanding the physical properties of rare gas systems under high pressure [42, 69, 71–73]. In particular, Schwerdtfeger and co-workers [42, 74] derived the volume and temperature dependence of the pressure—\( P(V, T) \)—for both Ne and Ar crystals from the Helmholtz free energy, which consists of a static term determined from many-body expansion based on the CC theory and a dynamical term determined from lattice vibrations. While excellent agreement with experiment was found for Ne up to 200 GPa [74], a comparable level of agreement was only achieved up to 20 GPa for Ar at room temperature [42]. In the pressure range of 20–100 GPa, appreciable discrepancy between calculated results and experiment was observed. As such, a theoretical description of the equation of state at high pressure reaching the experimental accuracy was considered to be a significant challenge for the Ar crystal [42].

To check how RPA+rSE performs in the high-pressure regime, we here also determine the equation of state \( P(V, T) \) from the Helmholtz free energy via \( P(V, T) = -\frac{\partial F(V, T)}{\partial V}_{|T} \), whereby the expression of the Helmholtz free energy is presented in section 2 (equation (6)). In brief, the static part of the Helmholtz energy in our calculations is given by RPA+rSE total energy, whereas the ZPE and lattice thermodynamic vibration contributions are determined from the phonon spectrum based on PBE calculations. The possible influences of the underlying XC functional for evaluating the phonon spectra on the obtained \( P-V \) curve and on the Helmholtz free energies themselves are examined in figures S4 and S5 of the SM, respectively. There one can see again that varying the functional has negligible impact. In figure 3, our calculated \( P-V \) results as a function of \( V \) at \( T = 300 \) K are presented for the fcc phase of the Ar crystal. For comparison, the calculated results of Schwerdtfeger et al [42] as well as the experimental results [75–77] are also included. To stay away from the melting point (the melting pressure \( P_{\text{mel}} \) and volume \( V_{\text{mel}} \) at 300 K are estimated to be 1.353 GPa and 32.64 Å³ in references [78, 79]), only the compressed volume regime with \( V < 32 \) Å³ was considered in our investigation. Figure 3 shows that our calculated \( P-V \) results are in very good agreement with the experimental data of Ross et al [77] extracted from static pressure measurements and of Errandonea et al [76] extracted from dispersive x-ray diffraction measurements up to 50 GPa. In addition to the fcc phase, we also calculated the \( P-V \) curve in the high-pressure regime for the hcp phase, but its difference from that of the fcc phase in the scale of figure 3 is tiny. Overall, it seems that our approach
Figure 3. Calculated $P$–$V$ diagram at 300 K for the fcc phase of the Ar crystal. Calculations are done using the six-atom supercell (as figure 2) and the results are extrapolated to the CBS limit. We choose RPA+rSE accomplished with phonon free energy at 300 K in our work here (green line). Theoretical results of reference \[42\] obtained using many-body expansion and the experimental data taken from references \[75–77\] are included for comparison.

describes the equation of states in high-pressure regime rather well, in contrast with the CC-based many-body expansions. Schwerdtfeger et al \[42\] attributed the disparity of their results from experiment to the missing four-body and higher body effects within their approach and the possible inaccuracy of CCSD(T). In our case, RPA+rSE is less accurate than CCSD(T), but our calculations account for the many-body effects to infinite order. From this perspective, we propose that it is most likely not the method of CCSD(T) itself, but rather the limited order of the many-body expansion that is responsible for the discrepancy observed by Schwerdtfeger et al \[42\].

3.4. The $T$–$P$ phase diagram for Ar

Figure 2 signifies that at zero temperature the fcc phase can transform into the hcp phase at a compressed volume of approximately 17 Å$^3$ per atom, corresponding to a pressure of 31.4 GPa, as can be inferred from figure 3. To investigate how the transition pressure changes with the temperature, we calculate the Gibbs free energies $G(T,P)$ for both phases at several different temperatures, and pinpoint the boundary between the two phases in the $T$–$P$ phase diagram by equating the Gibbs free energies of the two phases $G_{fcc}(T,P) = G_{hcp}(T,P)$. The resultant $T$–$P$ phase diagram is presented in figure 4, where the boundary line is determined by data points at seven different temperatures ranging from 0 to 300 K. One can see that the transition pressure increases steadily from 31.4 GPa at 0 K to about 37.0 GPa at 300 K. In table SI of SM, we present the actual values of the critical pressure and volume along the phase boundary line. The steady increase of the transition pressure along with the temperature is related to the different phonon spectra of the two phases. The lattice vibrations are such that the higher-symmetry phase (fcc) is favored over the lower-symmetry phase at finite temperatures, and thus a higher pressure is needed to turn the fcc phase into the hcp one, compared to the zero temperature case. Close inspection reveals that the positive slope of the phase boundary is related to the slightly larger entropy and volume of the fcc phase than the hcp phase under the same temperature and pressure conditions. Namely, the positive sign of $\Delta S/\Delta V$ across the phase boundary line gives rise to a positive $dP/dT$ slope, according to the Clausius–Clapeyron relationship (i.e., $dP/dT = \Delta S/\Delta V$) for a solid–solid phase transition.

Experimentally, Errandonea et al observed that a phase transition from fcc to hcp starts at 49.6 GPa under room temperature \[76\], and after that the two phases coexist over a wide pressure range. Determining the hysteresis region between the two solid-state phases requires a rather long-time NPT molecular dynamics simulations and goes beyond the scope of the present work. Quantitatively, our simulation seems to underestimate the transition pressure, but nevertheless predicts the correct order of
Figure 4. The $T$–$P$ diagram of the Ar crystal, where the phase boundary between the fcc and hcp phases are determined by the Gibbs free energy. Calculations are done using the six-atom supercell model at several successive temperatures, i.e., 0, 50, 100, \ldots, 300 K. Both electronic (RPA+rSE) and phonon (PBE) parts of the Gibbs free energy are extrapolated to the CBS limit [CBS(3, 4)].

magnitude for the transition pressure. Several factors might contribute to this underestimation. First, in the present work, the ideal structure is used for both the fcc and hcp phases, whereas in reality disorder and defects play important roles. Second, the dynamics of the phase transition process is rather complex, governed by a delicate interplay between energetics and kinetics, as, e.g., discussed in references [73, 80] for the martensitic fcc–hcp transition in solid xenon. These aspects have not been taken into account in our studies, but needs to be taken into account to achieve a quantitatively accurate description of the detailed phase transition behavior.

4. Conclusion

To summarize, we carried out a first-principles study of the energy difference and the transition between the fcc and hcp phases of the Ar crystal. The electronic part of the free energy is calculated at the level of RPA plus renormalized singles corrections [30], and the ZPE and thermodynamic lattice vibrations are determined at the PBE level using the harmonic approximation. Our results show that, at zero temperature, RPA+rSE predicts that the fcc structure has a lower energy than the hcp structure at ambient and high pressures up to 30 GPa. The ZPE slightly favors the fcc structure over the hcp one, but its effect is rather tiny and one order of magnitude smaller than the electron correlation effect described by RPA+rSE.

Computationally, in order to capture the delicate energy difference between the two phases, it is important to treat the fcc and hcp structure on an equal footing, i.e., adopting the same computational unit cell and parameters for both structures.

In the high-pressure regime, our $P$–$V$ curve is in excellent agreement with available experimental data. Such an agreement is not achieved with the CC-based many-body expansion approach, and has been regarded as a significant challenge for theoretical methods [42]. Based on our results, we propose that the inadequacy of the many-body expansion approach is probably due to the missing four- and higher-body terms, and not due to the CCSD(T) method itself. By computing the Gibbs free energies for both phases, we are able to determine a $T$–$P$ phase diagram of the Ar crystal. Although the transition pressure is somewhat underestimated and no details of the transition process is provided yet, determining a qualitatively correct phase diagram for the Ar crystal entirely from first principles itself is a great success. We believe our findings presented in this work will have significant implications for investigating other rare-gas systems and more complex materials in general.
Acknowledgments

The work is supported by National Natural Science Foundation of China (Grant No. 11874335), and Max Planck Partner Group for Advanced Electronic Structure Methods. We thank Igor Ying Zhang and Xinzheng Li for helpful discussions.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: 10.17172/NOMAD/2021.12.06-1.

ORCID iDs

Xinguo Ren https://orcid.org/0000-0002-3360-2281

References

[1] Maddox J 1988 Nature 335 201
[2] Wille L T 1987 Chem. Phys. Lett. 133 405
[3] Wales D J and Doye J P K 1997 J. Phys. Chem. A 101 5111–6
[4] Deaven D M and Ho K M 1995 Phys. Rev. Lett. 75 288–91
[5] Glass C W, Oganov A R and Hansen N 2006 Comput. Phys. Commun. 175 713–20
[6] Wang Y, Hu J, Zhu L and Ma Y 2010 Phys. Rev. B 82 094116
[7] Burke K 2012 J. Chem. Phys. 136 150901
[8] Jones R O 2015 Rev. Mod. Phys. 87 897–923
[9] Heyd J, Scuseria G E and Ernzerhof M 2003 J. Chem. Phys. 118 8207
[10] Sun J et al 2016 Nat. Chem. 8 831
[11] Lejaeghere K et al 2016 Science 351 aad3000
[12] Marzari N, Ferrer A and Wolverton C 2021 Nat. Mater. 20 736
[13] Klein M and Venables J 1976 Rare Gas Solids (London: Academic)
[14] van de Waal B W 1991 Phys. Rev. Lett. 67 3263–6
[15] Kohn W and Sham L J 1965 Phys. Rev. 140 A1133
[16] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865
[17] Becke A D and Johnson E R 2007 J. Chem. Phys. 127 124108
[18] Grimme S, Antony J, Ehrlich S and Krieg H 2010 J. Chem. Phys. 132 154104
[19] Tkatchenko A and Scheffler M 2009 Phys. Rev. Lett. 103 073005
[20] Tkatchenko A and Scheffler M 2012 Phys. Rev. Lett. 108 236402
[21] Dion M, Rydberg H, Schröder E, Langreth D C and Lundqvist B I 2004 Phys. Rev. Lett. 92 246401
[22] Klimel J, Bowler D R and Michaelides A 2010 J. Phys.: Condens. Matter. 22 022201
[23] Perdew J P and Schmidt K 2001 Density Functional Theory and its Application to Materials ed V Van Doren, C Van Alsenoy and P Geerlings (New York: AIP)
[24] Bohm D and Pines D 1953 Phys. Rev. 92 609
[25] Langreth D C and Perdew J P 1977 Phys. Rev. B 15 2884
[26] Gunnarsson O and Lundqvist B I 1976 Phys. Rev. B 13 4274
[27] Eshuis H, Bates J E and Furche F 2012 Theor. Chem. Acc. 131 1084
[28] Ren X, Rinke P, Joas C and Scheffler M 2012 J. Mater. Sci. 47 7447
[29] Ren X, Rinke P, Blum V, Wienerink J, Tkatchenko A, Sanfilippo A, Reuter K and Scheffler M 2012 New J. Phys. 14 053020
[30] Ren X, Rinke P, Scuseria G E and Scheffler M 2013 Phys. Rev. B 88 035120
[31] Møller C and Plesset M S 1934 Phys. Rev. 46 618
[32] Bartlett R J and Musial M 2007 Rev. Mod. Phys. 79 291
[33] Hermann A and Schwedtfeger P 2009 J. Chem. Phys. 131 244508
[34] Casassa S, Halo M and Maschio I 2008 J. Phys.: Conf. Ser. 117 012007
[35] Schwedtfeger P, Assadollahzadeh B and Hermann A 2010 Phys. Rev. B 82 205111
[36] Head-Gordon M and Pope J A 1988 J. Chem. Phys. 89 5777
[37] Lotrich V F and Szalwicz K 1997 Phys. Rev. Lett. 79 1301–4
[38] Roisiciszewski K, Paulus B, Fulde P and Stoll H 2000 Phys. Rev. B 62 5482–8
[39] Roisiciszewski K, Paulus B, Fulde P and Stoll H 1999 Phys. Rev. B 60 7905–10
[40] Schwedtfeger P, Tonner R, Moyano G E and Pah H 2016 Angew. Chem., Int. Ed. 55 12200–5
[41] Schwedtfeger P, Gaston N, Krawczyk R P, Tonner R and Moyano G E 2006 Phys. Rev. B 73 064112
[42] Schwedtfeger P, Steenbergen K G and Pah H 2017 Phys. Rev. B 95 214116
[43] Dobson J F 1994 Topics in Condensed Matter Physics ed M P Das (New York: Nova)
[44] Scuseria G E, Henderson T M and Sorensen D C 2008 J. Chem. Phys. 129 231101
[45] Lebegue S, Harl J, Gould T, Ángyán J G, Kresse G and Dobson J F 2010 Phys. Rev. Lett. 105 196401
[46] Zhang M Y, Cui Z H and Jiang H 2018 J. Mater. Chem. A 6 6606–16
[47] Cazorla C and Gould T 2019 Sci. Adv. 5 eaau5832
[48] Sengupta N, Bates J E and Ruzsinszky A 2018 Phys. Rev. B 97 235136
[49] Furche F 2001 Phys. Rev. B 64 195120
[50] Harl J, Schimka L and Kresse G 2010 Phys. Rev. B 81 115126
[51] Ren X, Tkatchenko A, Rinke P and Scheffler M 2011 Phys. Rev. Lett. 106 153003
[52] Paier J, Ren X, Rinke P, Scuseria G E, Grüneneis A, Kresse G and Scheffler M 2012 New J. Phys. 14 043002
[53] Klimeš J, Kaltak M, Maggio E and Kresse G 2015 J. Chem. Phys. 143 102816
[54] Blum V, Hanke F, Gehrke R, Havu P, Havu V, Ren X, Reuter K and Scheffler M 2009 Comput. Phys. Commun. 180 2175
[55] Heßelmann A and Görling A 2011 Mol. Phys. 109 2473
[56] Rézač J, Riley K E and Hobza P 2011 J. Chem. Theory Comput. 7 2427–38
[57] Tahir M N, Zhu T, Shang H, Li J, Blum V and Ren X 2021 Localized resolution of identity approach to the analytical gradients of random-phase approximation ground-state energy: algorithm and benchmarks (arXiv:2109.00742)
[58] Ihrig A C, Wieferink J, Zhang I Y, Rope M, Ren X, Rinke P, Scheffler M 2015 New J. Phys. 17 093020
[59] Ren X, Merz F, Jiang H, Yao Y, Rampp M, Lederer H, Blum V and Scheffler M 2021 Phys. Rev. Mater. 5 013807
[60] Zhang I Y, Logsdail A J, Ren X, Levchenko S V, Ghi ringhelli L and Scheffler M 2019 New J. Phys. 21 013025
[61] Zhang I Y, Ren X, Rinke P, Blum V and Scheffler M 2015 New J. Phys. 17 123053
[62] Helgaker T, Klopper W, Koch H and Noga J 1997 J. Chem. Phys. 106 9639–46
[63] Togo A and Tanaka I 2013 Scr. Mater. 108 1–5
[64] Perdew J P, Ernzerhof M and Burke K 1996 J. Chem. Phys. 105 9982
[65] Harl J and Kresse G 2008 Phys. Rev. B 77 045136
[66] Kresse G and Furthmüller J 1996 Phys. Rev. B 54 11169
[67] Schwalbe L A, Crawford R K, Chen H H and Aziz R A 1977 J. Chem. Phys. 66 4493–502
[68] Reichlin R, Brister K E, McMahan A K, Ross M, Martin S, Vohra Y K and Ruoff A L 1989 Phys. Rev. Lett. 62 669–72
[69] Ross M, Boehler R and Söderlind P 2005 Phys. Rev. Lett. 95 257801
[70] Ishikawa T, Asano M, Suzuki N and Shimizu K 2015 Phys. Rev. B 91 064512
[71] Kwon J, Collins L A, Kress J D and Troullier N 1995 Phys. Rev. B 52 15165–9
[72] Dewhurst J K, Abruha R, Li S and Johansson B 2002 Phys. Rev. Lett. 88 075504
[73] Kim E, Nicol M, Cynn H and Yoo C S 2006 Phys. Rev. Lett. 96 035504
[74] Schwedtfeger P and Hermann A 2009 Phys. Rev. B 80 064106
[75] Finger L, Hazen R, Zou G, Mao H and Bell P 1981 Appl. Phys. Lett. 39 892
[76] Errandonea D, Boehler R, Japel S, Mezouar M and Benedetti L R 2006 Phys. Rev. B 73 092106
[77] Ross M, Mao H, Bell P and Xu J 1986 J. Chem. Phys. 85 1028–33
[78] Wiebke J, Pahl E and Schwedtfeger P 2013 Angew. Chem., Int. Ed. 52 13202–5
[79] Kechin V V 2001 Phys. Rev. B 65 052102
[80] Cynn H, Yoo C S, Baer B, Iota-Herbei V, McMahan A K, Nicol M and Carlson S 2001 Phys. Rev. Lett. 86 4552–5