Influence of shell effects on thermodynamic properties of matter at high pressures

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Abstract. We analyze the influence of shell effects on thermodynamic properties of matter at high pressures. Spherically symmetric average atom models show significant contribution of electronic transitions to cold pressure which is not confirmed by more accurate density functional theory models. In particular, the $s$–$d$ transition in aluminum and potassium does not reveal itself on the shock Hugoniot. Oscillations on shock Hugoniot at very high pressures predicted earlier by many authors should be confirmed by precise first-principle calculations.

1. Introduction

Thermodynamic properties of matter at high pressure are of importance in many problems of high energy density physics, in particular, in astrophysics \cite{1}, in wide-range equations of state \cite{2, 3}, in the problems of interaction of intense energy fluxes with matter \cite{4–6}, in perspective power generation facilities \cite{7} and in some others. The finite-temperature Thomas–Fermi (TF) model \cite{8} based upon semiclassical approximation is widely used to describe thermodynamic properties of matter, but there are many phenomena beyond this approach. In particular, shell effects reflect non-regularities of physical parameters because of the discrete energy spectrum. For example, in low-density plasma step-wise dependencies of thermodynamic functions on isochors or isobars are quite typical \cite{9}. The other well-known effect is connected with the non-regular behavior of density of elements vs. atomic mass \cite{10, 11}. To describe shell effects one should take into account discrete energy levels. Analytically shell corrections to the TF model have been studied in \cite{12, 13} using the Poisson formula in the transition from summation to integration (see also the review \cite{14}). Average atom models \cite{15–19} are based on a radial solution of the single-particle Schrödinger (Dirac) equation so that the discrete spectrum and shell effects are taken into account implicitly. During the last 30 years it became possible to obtain approximate three-dimensional (3D) solutions of a quantum many-particle problem using density functional theory (DFT) \cite{20, 21}. In this case one gets a 3D band structure of a system of particles that provides for the appearance of shell effects through non-regularities of the electronic density and some thermodynamic functions. There were several attempts to register shell effects at high pressures and temperatures experimentally \cite{22–24} using underground nuclear explosions. It is claimed \cite{24} that the influence of the discrete energy spectrum is
Figure 1. Cold curve of potassium. Black solid line—average atom model [15]; red dashed line—all-electron DFT simulation for bcc lattice [33]; blue dash-dotted line—all-electron DFT simulation for fcc lattice [33]. Experimental data at 300 K: red circles—for bcc potassium; blue triangles—for fcc potassium; magenta-and-white circles—for potassium with Rb-IV crystal structure [34].

Indeed present at pressures about 1 TPa. Heuristically it seems that the 3D DFT model of matter is more realistic than the average atom one as in the last case only radial dependences of electronic density and wave functions are considered. In this work we analyze the magnitude of shell effects at high pressures and low temperatures predicted by different models. The situation at high pressures and temperatures is also discussed.

2. Methods of calculation

We use the plane-wave pseudopotential code VASP [25–27] which realizes the finite-temperature DFT formalism. Projector-augmented wave (PAW) pseudopotentials [28] and the generalized gradient approximation (GGA) with Perdew–Burke–Erzenhof (PBE) [29,30] corrections for the exchange-correlation functional are applied in all simulations. Parameters of simulations (the number of \( \mathbf{k} \)-points, the plane-wave cutoff energy and others) were adjusted to reach convergence of results. At zero temperature a traditional DFT approach is applied: the distribution of electronic density is calculated in an elementary cell with immovable ions. At \( T > 0 \) the quantum molecular dynamics (QMD) method allows us to simulate a cubic supercell with up to 1000 ions; in the Born–Oppenheimer approximation quantum electrons are treated by DFT while the movement of classical ions obeys Newton’s second law. As some electrons in a pseudopotential DFT approach are included into an invariable core this method is restricted both on temperature and density because of the excitation of core electrons [31]. Also in QMD additional error may appear when some particles move very close to each other at high enough temperatures [32]. Therefore the validity of each pseudopotential should be checked at given simulation conditions.
3. Results and discussion
The influence of shell effects on thermodynamic functions at high pressures are usually connected with the excitation of electrons of an atom under pressure or temperature. For example, in potassium the so-called s–d transition at cold compression was predicted [10, 38] in which the outer 4s electrons occupy the empty 3d band. The mutual arrangement of the bands also changes: the bottom of the 3d band under pressure shifts to lower energies than the bottom of the 3s one. This transition may affect the cold curve and shock Hugoniot of potassium. Indeed, an oscillatory character of the cold curve of K was obtained by the average atom model [15]: a van-der-Waals character of the isotherm was noted in the pressure-specific volume plane. The s–d transition is valid for all alkali metals, so the rearrangement of electrons between the bands takes place indeed. However, in 3D simulations structural phase transitions under pressure are possible; also the electrons have more spatial degrees of freedom in 3D than in the radially-symmetric case. Therefore the manifestation of the s–d transition may be much less than predicted by average-atom models.

In figure 1 the results for cold compression of potassium are shown. In experiment at room temperature [34] it was revealed that potassium has two structural phase transitions under pressure: bcc-fcc at 11 GPa and fcc-Rb-IV at 19 GPa. In the last transition the change of density is about 4.1%. DFT calculations of cold curves of bcc and fcc potassium performed with the full-potential code [33, 39] are almost coincide up to very high pressures and have very slight oscillations caused by the s–d transition. Simulation of the Rb-IV phase with 16 atoms in the elementary cell is very complicated, that is why the effect of the s–d transition on the cold curve of potassium with the Rb-IV crystal structure is currently unknown, but almost certainly small. The maximum on the cold curve of potassium by the average atom model [15] contradicts the experimental data for Rb-IV [34] which demonstrate a steady increase of pressure under compression.

Figure 2. Experimental shock Hugoniot data (squares—[35]; circles—[36]; triangles—[37]) and theoretical cold curve results (black solid line—[15]) for potassium.
Figure 3. Cold curve of aluminum. Black solid line—average atom model [15]; red solid line—QMD simulation, this work; black dashed line—full-potential DFT with mean-field potential [51]; white diamonds—equation of state based on DFT simulation [46]. Experimental data at 300 K: green circles—[52]; white triangles—[53]; white squares—[53] (for hcp aluminum).

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Figure 4. Shock Hugoniot of aluminum. Red solid line—QMD simulation, this work; black solid line—approximation of experimental data from [10]. Experimental data: black squares—[40]; black triangles—[41]; black diamond—[42]; white diamond—[43]; white triangles—[45]; white squares—[49].

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it is claimed that the TF model with quantum and exchange corrections is not able to describe experimental data within the experimental accuracy. On the other hand the average atom model [16] was in better agreement with the measurements, that is why it was declared about the experimental confirmation of shell effects manifestation on the shock Hugoniots of aluminum and lead [24]. It is important to note, however, that there is a significant discrepancy between different average atom models at pressures higher than 100 TPa; also the ionic contribution to pressure is noticeable and depends on the model [62]. In our opinion, the influence of shell effects on shock Hugoniots at very high pressure should be checked independently using a model which consistently takes into account both ionic and electronic contributions. One of such models is the direct path integral Monte Carlo (DPIMC) method [64] which strictly considers many-particle exchange and correlation effects. Unfortunately due to computational problems the DPIMC approach can be applied only to light elements such as hydrogen or helium. Nevertheless, it was demonstrated that shell effects on hydrogen isochors are caused by ionization and become less pronounced at higher interparticle interaction [65]. As density on a shock adiabat at very high pressures tends to a certain limit a shock-compressed system becomes less coupled with the rise of pressure. However, interaction effects are still quite strong in the region of shock-induced ionization in metals therefore first-principle simulations of shock Hugoniots may shed light on the magnitude of shell effects at very high pressures. Pronounced shell effects on the shock Hugoniot of sodium have been predicted recently using the restricted PIMC method [66]; however, this approach is based upon the single-particle fixed-node approximation which introduces an uncontrollable error to the results. Among other methods, QMD shows excellent

Figure 5. Atomic volumes of some elements (including all alkali metals up to Rb) at different pressures and zero temperature. Open circles—treatment of shock-wave data [10]; solid stars—DFT simulation. Individual colors correspond to different pressures: \( P = 0 \) (black), 10 (red), 100 GPa (blue) and 1 TPa (magenta). The lines only join the points and do not correspond to any dependence.
results for shock Hugoniots (see [50] and references therein) and melting curves [67, 68] of different materials at low and moderate pressures. At pressures higher than 100 TPa, however, a pseudopotential with at least 11 electrons is necessary to accurately take into account ionization of shocked aluminum. Such a calculation is challenging [69] as it requires very big cut-off energies and a huge number of plane waves.

4. Conclusion
Spherically symmetric mean atom models usually overestimates the influence of shell corrections on thermodynamic properties of matter at high pressures and low temperatures. The main reason of this fact is a much more complicated electronic structure of condensed matter in three dimensions in comparison with the radial symmetry one-dimensional case. The spatial redistribution of electron density in the interstitial region due to pressure or temperature effects may cause a structural phase transition or lead to much more regular dependencies of thermodynamic properties (such as pressure and energy). At high pressures and temperatures the influence of shell effects is probably determined by the coupling parameter: oscillations of thermodynamic functions are more pronounced for a more ideal system. Thus additional calculations are required to find out the scale of oscillations on shock Hugoniots at very high pressures.

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