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Equation of state of solid, liquid and gaseous tantalum from first principles

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ABSTRACT

We present ab initio calculations of the phase diagram and the equation of state of Ta in a wide range of volumes and temperatures, with volumes from 9 to 180 $Å^3$/atom, temperature as high as 20 000 K, and pressure up to 7 Mbars. The calculations are based on first principles, in combination with techniques of molecular dynamics, thermodynamic integration, and statistical modeling. Multiple phases are studied, including the solid, fluid, and gas single phases, as well as two-phase coexistences. We calculate the critical point by direct molecular dynamics sampling, and extend the equation of state to very low density through virial series fitting. The accuracy of the equation of state is assessed by comparing both the predicted melting curve and the critical point with previous experimental and theoretical investigations.

1. Introduction

The accurate determination of high-pressure and high-temperature equations of state (EOS) [1] and phase diagrams has fundamental importance in a wide variety of fields. For instance, geophysics and planetary sciences often require knowledge about the response of materials under extreme conditions [2]. There is also an increasing interest in modeling high-velocity impacts [3,4] via multiscale methods, which also demands EOS as fundamental input in a very wide range of conditions.

This paper presents comprehensive calculations of the EOS and the phase diagram of Ta. Our approach is built upon previous investigations [2,5,6] along four main dimensions. (i) It is based on direct ab initio calculations, without relying on any force-field fitting as a stepping stone. This enables us to assess the quality of these force fields concerned. (ii) It covers all phases, including the solid, liquid, and gas phases, and all associated two-phase equilibria. (iii) It includes the effect of electronic excitations. (iv) It delivers not only the phase diagram, but also the free energies of all phases, which serve as fundamental input in multi-scale or finite-element models. We obtain the free energy as a 2D function in a large section of the volume and temperature (V,T) space, with the associated pressure range of 0–7 Mbar, and the temperature range of 0–20 000 K, while the corresponding phases span from high-pressure dense liquids to gas states well beyond the critical point.

Transition metals are known to pose special challenges for density functional theory (DFT) [7–9], in terms of both computational accuracy and efficiency. However, for some transition metals (in particular Ta), the straightforward application of generalized gradient approximation (GGA) [10–12] was shown capable of delivering accurate solid properties and melting curve [2,13], despite the ongoing debates over issues such as the mismatch between diamond-anvil-cell (DAC) measurements and shock experiments data, as well as the possibility of polymorphism in high-pressure solids [14–16]. These previous studies suggest that it is within the reach of modern theory to accurately compute the thermodynamic properties of Ta at the atomistic scale, for a vast range of thermodynamic conditions up to very high pressures, temperatures, and volumes. Carefully constructed numerical procedures and techniques are capable of capturing the information implicitly present in the DFT Hamiltonian to compute thermodynamic functions of states.

To investigate the material behavior across various phases, we rely on a unifying approach of thermodynamic integration. Its most expensive part is the ab initio molecular dynamics (MD) sampling of local material properties at each point with fixed density and temperature, which needs to be independently collected on a 2D grid in the vast (V,T) region. To reduce the computational burden, we employ analytic statistical mechanics modeling where appropriate. This technique also provides a reference point for the integration and allows us to extrapolate

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beyond the directly calculated region.

Although DFT is now routinely used to calculate phase transitions in dense regions of the phase diagram [17], it is generally considered that it becomes less reliable for the gas phase, where atoms are separated by larger distances on average. The critical point (CP) of the liquid–gas phase transition is an important and universal feature of the EOS, positioned between typical dense solid/liquid region and the ideal gas limit, where first-principles data would be very useful [18]. However, as the CP arguably lies at the frontier of the traditional valid domain of DFT, it is necessary to perform a detailed investigation on a relevant system and to compare the results with experiments. One such system of interest is transition metals like Ta. Experimentally, the determination of critical point parameters (including critical pressure P_c, critical temperature T_c, and critical density here expressed as the critical volume per atom V_c) is a long standing open question for most metals [19], because P_c and T_c are too high to precisely study from experiments [18]. Although there have been a number of experimental and semi-empirical estimates [19–26], their discrepancies are considerable, and thus a fully ab initio approach is helpful to further clarify these results. Finally, if DFT alone can be employed to calculate CP parameters and its vicinity with reasonable effort, this approach can be generalized whenever a material is believed to be accurately represented within the DFT framework.

This paper is organized in the following way. The next section describes the basic technical setup of the work and outlines the thermodynamic integration procedure. Section 3 concentrates on the solid phase, and Section 4 on the fluid. Section 5 elaborates the melting curve calculation, and Section 6 deals with the investigation of the critical point and related issues. Finally in Section 7, discussions and conclusions are presented. 3D interactive figures of the pressure field (including the data set), as well as a movie of liquid Ta in MD, are available as supplementary materials.

2. AB initio methodology

All our calculations are based on ab initio DFT and performed with the VASP package [27]. We employ the projector augmented wave (PAW) technique [28] and a Perdew–Burke–Ernzerhof (PBE) [29] pseudopotential with the 5*p* core electrons relaxed, as such a setup was found satisfactory in previous work [2]. The package implements a finite-temperature formulation of DFT. The variational quantity that is minimized and kept constant throughout a *NVE* trajectory is the sum of the kinetic and potential energies and the electronic free energy of the system. Electronic excitation effects are included as the Fermi-type smearing of single particle energy level occupations, which corresponds to an electronic temperature T_e that is equal to the ionic temperature T_i calculated from the kinetic energy of ionic motion. In order to match T_e and T_i, we thermalized the system at a particular volume until the T_i coincided with the preset T_e within a small tolerance. All subsequent MD runs were performed within the *NVE* ensemble. The time step was chosen to be 2 fs, except at very low densities, where we could gradually increase it up to 6 fs without causing a significant drift in total energy. The lengths of data-gathering trajectories varied in a wide range of 1–20 ps, depending on the temperature, pressure, density, and local density of sampled points in the (V,T) space. The plane wave energy cutoff was set at 275 eV, providing a total energy error of no more than 7 meV per particle and a pressure error of less than 0.4% at high pressures. We have tested spin polarization effects and reconfirmed their irrelevance. The number of atoms in the simulation cell was 128, except when close to the gas phase, which will be discussed later in detail. The *k*-space sampling was performed using Monkhorst–Pack special points. In the solid phase, all MD runs were performed with a $2\times2\times2$ mesh. In the fluid, total-energy calculations was carried out on the $2\times2\times2$ mesh, while for pressure calculations the Γ-point setup was proven sufficient. In order to evaluate the finite-size effect, we performed tests on a system of 250 atoms at the point of the highest density and temperature, where insufficiencies of our setup were most likely to be noticed. These tests gave no significant change in results and suggested that the finite-size effect was small.

To construct the free energy of Ta in 2D space $F(V,T)$, we employ the method of thermodynamic integration, using the two thermodynamic relations [30]:

$$P = -\left(\frac{\partial F}{\partial V}\right)_T, \tag{1}$$

$$E = \left(\frac{\partial(F/T)}{\partial(1/T)}\right)_V, \tag{2}$$

where P is the pressure, and E the total kinetic and potential energy of the system calculated from MD. As a general procedure, we calculate pressures on a 2D grid of points, and energies on a 1D grid of points at a selected volume, as illustrated in Fig. 1. A fine grid is required so that the fitted analytic functions $P_f(V,T)$ and $E_f(T)$ are smooth and reliable. There exist multiple solutions for the $F_f(T)$ curve constructed by Eq. (2) and $E_f(T)$, because the thermodynamic relation is also satisfied by $F_f(T) - TS_0$ for any arbitrary entropy constant S_0. If this constant is known, the free energy F can then be fully determined anywhere in the (V,T) region of interest.

As explained later in the text, S_0 was conveniently determined by the knowledge of the melting point T_m, which can be calculated in a variety of ab initio approaches [2,5,6,30–33]. In the case of Ta, this problem was already studied with success. Hence we referred to previous ab initio-based theoretical calculations.

3. Solid phase

The body-centered cubic (BCC) phase of Ta is stable from zero temperature to melting at all volumes. The free energy per particle of Ta can be treated within the quasiharmonic approximation (QA) as

$$F_{QA}(V,T) = F_0 + \frac{E_0(V)}{N} + F_v(V,T) + F_e(V,T), \tag{3}$$

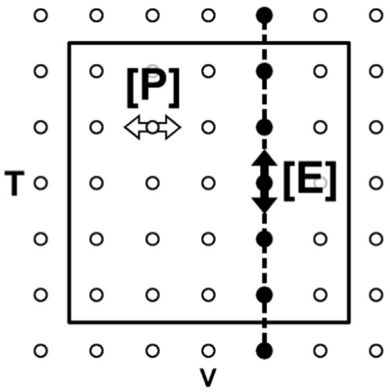

Fig. 1. Thermodynamic integration of the free energy in a finite region of two-dimensional (V,T) space. The pressure is calculated on a 2D grid of points along the horizontal direction (open arrows), while the total energy changes on an 1D grid of points, for integration in the vertical direction (solid arrows). To avoid extrapolation errors, the grid should fully encompass the selected region, shown as the square.