Computational Materials Science 156 (2019) 121–128

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

An automated algorithm for reliable equation of state fitting of magnetic systems

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ARTICLE INFO

Keywords:
Equation of state fitting
EOS

ABSTRACT

In computational physics and materials science ground-state properties are often extracted from an equation of state fit to energy-volume data. Magnetic systems often have multiple magnetic phases present in the energy-volume data, which poses a challenge for the fitting approach because the results are sensitive to the selection of included fitting points. This is because practically all popular equation of state fitting functions, such as Murnaghan and Birch-Murnaghan, assume just one phase and therefore cannot correctly fit magnetic energy-volume data that contains multiple phases. When fitting magnetic energy-volume data it is therefore important to select the range of fitting points in such a way that only points from the one relevant phase are included. We present a simple algorithm that makes the point selection automatically. Selecting fitting points automatically removes human bias and should also be useful for large-scale projects where selecting all fitting points by hand is not feasible.

1. Introduction

Experimentalists and theoreticians alike have always had a need for reliable equation of state (EOS) fitting functions. They serve several important purposes which are all well documented in the literature; for more information about EOS fitting the reader is referred to Ref. [1] and references therein. In this paper we focus on a use case which is especially popular in *ab initio* solid-state physics. In this use case ground-state properties of a solid are often obtained by computing the total energy of a solid for a range of consecutive volumes and then performing a least-squares fit to the energy-volume data using one of the EOS fitting functions.

Many different EOS functions based on different physical arguments and assumptions have been developed over decades. Already in 1944 Murnaghan [2] presented his formula for equation of state based on the exact treatment of finite deformation in elastic solids. Few years later Birch [3] improved his work and in 1987 Vinet et al. [4] proposed a universal expression for equation of state which works for ionic, metallic, covalent and rare gas solids. A year later Moruzzi et al. [5] investigated equation of state in finite temperatures. In 1997 Anton and Schmidt [6] studied bulk and shear moduli of metal compounds to investigate deviation of computational results from experiments. Poirier and Tarantola [7] introduced an improved Birch-Murnaghan equation of state for greated range of pressure in 1998. In the same year Holzapfel [8] discussed the physical and theoretical reasoning behind different equations of state and presented a new function called AP1. In 2001 Alchagirov et al. [9] presented their universal equation of state function called SJEOS motivated by stabilized jellium model. The thermal effects in equations of state were discussed in article by Hozapfel [10] in 2002.

Traditional EOS functions usually assumes single-phase data or good quality of data without jumps and kinks. Unfortunately single phase cannot always be guaranteed or data can contain jumps because of failed experiments or computations. In 2011 Otero-de-la-Roza and Luaña [1] discussed the problem of noise and jumps in the data for the equation of state fitting and introduced a simple way to detect and remove jumps from the data. More recently, in 2015 Cox and Christie [11] wrote an article about using swarm intelligent fitting for multi-phase equation of state. In their article they used particle swarm optimization to fit equation of state data across multiple phases with good agreement.

Magnetism, for example, can cause problems for EOS functions.

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https://doi.org/10.1016/j.commatsci.2018.09.026
Received 25 July 2018; Received in revised form 11 September 2018; Accepted 13 September 2018

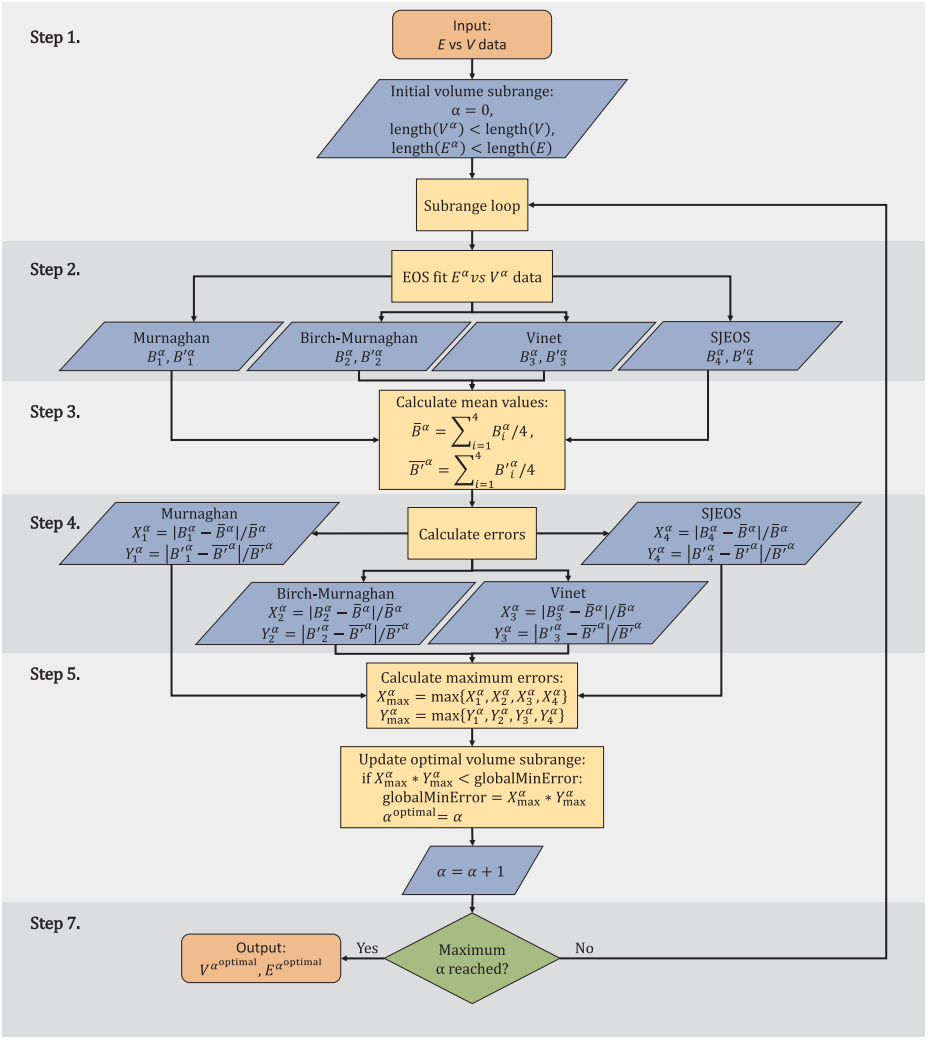

Fig. 1. Flowchart of the AEOS algorithm.

Fitting magnetic energy-volume data is challenging because volume dependent magnetic transitions often introduce more than one phase, which manifest as kinks (Fig. 2, upper left panel) and jumps (Fig. 2, upper right panel) in the energy. The multi-phase nature of magnetic energy-volume data makes their EOS fitting a nontrivial procedure, because EOS functions are designed to fit single-phase energy-volume data and are not designed to take into account kinks and jumps that may be present. This problem shows up especially in the more sensitive quantities that are extracted from the fit; the bulk modulus $B(V) = V(\partial^2 E)/(\partial V^2)$ is one good example. The value of the bulk modulus depends heavily on which points are included in the fit. Pure iron is a good example of this phenomenon [12]. The calculated bulk modulus of iron shows significant scatter in the literature, which is because the volume range has not been the same for the different fits. For the most reliable bulk modulus, as well as other quantities, the volumes that are included in the fit should be chosen in such a way that all — or as many as possible — volumes used in the fit correspond to the same phase.

In this paper we present a simple algorithm that can be used to make the selection of fitting points automatically. There already exists approaches that can automatically detect noise, outliers, and small jumps [1], but the purpose of our algorithm is to automatically narrow the whole volume range down to a smaller range that produces the most reliable fitting results for magnetic systems. Our algorithm is useful in two ways. Firstly, it removes the human element. It could be argued that picking fitting points by hand can be a source of bias because sensitive quantities, such as bulk modulus, are easily tuned by choosing a particular volume range.

Secondly, reliable automation of EOS fitting is welcome in large scale projects that involve more EOS fits than can feasibly be taken care of by hand. Typical project could involve material informatics [13,14], like the Materials Project [15]. The material informatics is an emerging field mixing (computational) material science with informatics to discover new materials. To benefit most from the material informatics one needs good descriptors [13,16–18] of materials, an analysis framework [17,19,20] and a large database with reliable data. In the last part the automation of EOS fitting becomes most welcome. Another use of automatic EOS fitting is in automation of high performance computations, like project AiiDA [21].

It should be noted that fitting problems are to some extent artificial and caused by the approximations used in calculations. For example, in some cases spin-fluctuation theory [22,23], which produces more realistic and smoother magnetic transitions, can be used to obtain energy-volume data that is much easier to fit reliably. But the careful selection of fitting points is certainly faster and easier than performing spin-fluctuation calculations, and therefore should be of great interest. It should also be noted that our algorithm is general and can be used in conjunction with transitions other than just the magnetic ones. In this paper, however, we focus on magnetic transitions, because they are a very common headache when EOS fitting *ab initio* energy-volume data. The algorithm presented in this paper could also prove to be useful for fitting pressure-volume data, but this is a subject of a future work.