Statement of Interest

First Principles approaches for calculation of Equations of State, from Ideal to Real.

INTRODUCTION

First principles electronic structure calculations have recently reached a level of accuracy and predictive power that allows us to compute Equations of State (EOS) in a systematic way without having to resort to uncontrolled approximations. Since these schemes are based in fundamental physics and well defined approximations, there are no fitted parameters. This results in an approach that has a great deal of predictive power which has proved to be an extremely useful complement to experimental investigations, as well as for exploring states of matter where experimental measurements do not yet exist.

The design of dynamic high-pressure experiments requires the use of hydrodynamic simulations in which materials are subject to large pressure and temperature gradients, and the resulting response of the materials is computed with the relevant fluid transport equations. The accuracy of a hydrodynamic simulation depends critically on the quality of the EOS tables used as input. Another discipline that makes intensive use of EOS is planetary modeling. Accurate phase diagrams for simple molecular fluids and their constituent elements are important for constructing planetary models of giant planets. Having inaccurate EOS or phase lines can severely undermine the utility of the hydrodynamic approach and the underlying engineering projects and planetary models.

The focus of this proposal is to fill the existing gap between the recent and sustained development of first principles calculations and EOS tables efforts. The proposed research will enable the construction of highly accurate EOS tables for materials of interest, which in turn have a direct impact on many ongoing projects that require high quality hydrodynamic modeling.

BACKGROUND

A general approach that is currently being used in the EOS tables development is based in the computation or experimental measurement of cold curves, together with an electron-thermal part using Thomas-Fermi theory and an ion-thermal part described by the Debye-Gruneisen model. Melting lines are computed roughly based on Lindemann melting criterion. This combination of approximations can be considered a "top-down" approach, because while it matches well with the plasma and high compression limits, the low temperature side is usually described only approximately in an ad hoc manner. This general approach is very efficient and can cover elements in the whole periodic table. However, there are some select cases where a more detailed and accurate description is needed.

The problem arises when we move down into the realm of condensed matter, in particular when we need to describe solid-solid or solid-liquid transitions in detail.

The condensed matter limit requires a different level of description. My proposal aims to complement the "top-down" approach with a "bottom-up" description which can describe EOS in the low and moderate temperatures range, i.e. near the relevant solid-solid and solid-liquid transitions.

The design of capsules for Inertially Confined Fusion (ICF) during the National Ignition Campaign (NIC) is a clear example of an application in need for a good "bottom-up" description for a specific set of materials. The capsule design is driven by the need of avoiding hydrodynamic instabilities upon the first stages of shock compression. There are several candidate materials for making these ignition capsules, among them, Beryllium and High Density Carbon (HDC). Due to the specific properties of each material, the current strategies for avoiding hydrodynamic instabilities are somewhat different. In the case of Beryllium, it will be necessary to ensure that the first shock completely melts the capsule material; while in the case of HDC the approach is to produce a first shock that can significantly compress and heat the material without melting it. Note that in order to achieve these design goals, one must have a precise knowledge of the phase diagram and the EOS of the materials involved.

FROM IDEAL TO REAL

My proposal focuses on the implementation of an integral approach for elucidating the properties of materials and their EOS. In particular, I propose to use a combination of first principles calculations to give an overall description of the condensed matter domain, including solid-solid transitions at finite temperature, and melting lines.

A key component of the EOS is the one corresponding to the solid phases. The proposed approach will allow the computation of EOS cold curves that include full ionic quantum effects (zero point energy), which are critical, for example, when describing the low temperature initial condition in shock experiments. Previous work demonstrated that it is also feasible to extract anharmonic effects and its implications to the EOS from first principles molecular dynamics.

Melting lines can be computed by the two-phase method. The two-phase method is based on the direct simulation of the solidification and melting processes by starting from an initial condition that has both the solid and the liquid in the same simulation cell. By following the evolution of the solid-liquid interface at a given temperature and pressure, one can determine which is the most stable phase under such conditions. Of note is that this scheme does not require the direct calculation of the free energy, but it can be of paramount utility for calculating it, as I will describe later. In principle, there is no intrinsic limitation in this approach, as long as the stable solid phases are known. The stable solid structure can be inferred from experimental results, or it can be solved in a purely ab initio context.

Finding the stable solid phase at a given pressure and temperature is a hard (combinatorial) problem that has been unsolved for many years. The

multidimensional nature of the problem and the existence of local minima has motivated the use of a number of different stochastic global search strategies. For example, Oganov et al. recently demonstrated that evolutionary algorithms can be used to predict the crystal structure on systems with up to 80 atoms per unit cell, including compounds and multi-stoichiometric alloys.

It is possible to make the algorithm concentrate on the most promising area of the configuration space until the global minimum is found, by selecting only the best individuals (less energetic) in a fictitious population of structures, and combining them to produce the next generation of structures. In order to increase efficiency, I propose to use multiple levels of theoretical approximations to the total energy; as the algorithm approaches the minimum it can switch to more accurate methods of calculating the energy. We can incorporate algorithms of this kind in this project to predict the crystal structure in cases where experimental crystallographic information is not available.

Once the melting lines for each stable solid phase are determined (e.g. by the two-phase method), they can be used to exactly describe the free energy of the liquid without making additional hypothesis or introducing additional approximations. Because the free energy of the solid and the liquid are equal at the melting line, and the free energy of the solid is well known as described above, the melting line can be effectively used as a reference state for thermodynamic integration at higher temperatures. All the points along the melting line are valid as reference state, making the computation of liquid free energy very straight forward.

One of the current practical limitations in building EOS is the lack of a universal EOS for liquids. The first steps in this direction has been proposed by Chisolm et al.; however, there is a real need to develop more realistic models for the liquid. One of the goals of this project will be to investigate the possibility of devising new universal EOS for liquid that can be validated by first principles simulations. For example, molecular dynamics of liquids can provide information such as the coordination number, that can be used as a guide for identifying pressure ranges of simple behavior for the EOS. These pressure ranges can be patched together in a smooth way by using the coordination number fractions.

The overall proposed scheme can predict a global equation of state of the relevant stable solid and liquid phases. When the scheme is complemented with available experimental information, it can be used to estimate realistic error bars for predicted EOS and error propagation across description levels (e.g. along a hydrodynamic simulation). The aim will be to incorporate methods with a higher level of accuracy beyond Density Functional Theory (DFT), such as Quantum Monte Carlo (QMC), into the EOS table generation when applicable. For instance, QMC could be used to obtain better predictions of a material's cold curve. Part of the design goals of the project will focus on combining and handling a hierarchy of theories into the EOS construction.

Besides the equilibrium EOS, transport coefficients can be also computed within the same first principles framework. These include electrical conductivity, thermal conductivity and viscosities. I propose to calculate the transport properties within the same underlying approximations. This is of key relevance, since a uniform first principles theory is a necessary condition for achieving thermodynamic consistency. The framework proposed here provides the most predictive parameter-free scheme feasible with the current computational power and the current understanding of condensed matter physics by characterizing solid and liquid phases within a consistent description.

Real world materials possess a more complicated behavior than the one described by simple equilibrium EOS. For example, real materials have strength and can show large hysteresis in solid-solid transitions. A well established equilibrium EOS can actually isolate these second order effects in a clear way, as recently demonstrated by Orlikowski et al. In that work, a theoretical EOS allowed experimentalists to show anomalous behavior in the strength of HDC in Hugoniot experiments, something that without a good understanding of the EOS could have been absorbed in the equilibrium part.

The main approximations that will be used in this project (Density Functional Theory in the Generalized Gradient Approximation) have a range of validity that can be extended by using other theories. Thomas-Fermi theory and current implementations such as Inferno and Purgatorio can be used to extend the range of validity of the EOS by matching free energies at intermediate temperatures continuously. One of the goals of this project will be to connect these two limits (condensed matter and plasma) in a systematic and smooth way.

TECHNICAL DETAILS

The core of the project proposed here requires the development of a computer program that can automatize the EOS table generation. This program will have the ability to manage and work on top of implementations of electronic structure first principles codes such as ABINIT, PWSCF, QBOX and VASP. Each of these codes are particularly efficient for certain steps described in this project. An efficient use of them will require a flexible integration scheme. For example, one of the codes could be dedicated to find a good harmonic free energy for the solid, while a different one can be use to bracket the melting lines or estimate anharmonic effects in the solid. The results of this set of first principles calculations are going to be managed by a program that will integrate the large volume of data that is produced in order to construct an EOS.

I propose the option of having the results as (simple) analytic formulas that can be either inlined in hydrodynamic codes or tabulated to keep the full amount of information provided by the first principles results. This is related to the challenge of finding good analytic models that can describe the liquid state.

Finally, I am planning to give the eventual new EOS results immediate applications when possible, for example, by looking at consequences in the current planetary models. To give an extreme example, most extrasolar planets discovered to date are giant planets with interior conditions reaching pressures and temperatures as high as ~0.1-1Gbar and ~10,000K. Predictive models for these planets require in first place knowledge of EOS of the hypothetical constituents.

CONCLUSIONS

In summary, the project that I am proposing will integrate diverse first principles codes and implementations, EOS table construction routines and interfaces to hydrodynamic codes. I believe that Livermore Laboratory is the ideal place to pursuit this project due to the combination of expertise (both in theory and experiment), computational resources and the shear number of end-users that will immediately benefit from this project.

I anticipate that this project will involve a large degree of interaction between the groups in the Physical Sciences H and V Divisions, as well as the different hydro-code groups in the W&CI and NIF&PS programs. The Quantum Simulations Group would be the ideal host for my research.

I believe that the completion of this project will lead to great improvements in the process of constructing EOS. In particular, it is important to note that (i) all the steps proposed here are very robust, i.e. that in principle should be applicable to any substance and complex mixture (ii) each of these techniques has been validated by experiments and other complementary techniques (iii) it has been shown to be feasible with the computational power available in Livermore Laboratory and (iv) it will provide a consistent, well grounded description for EOS table construction.

In my opinion, the integration of methods proposed here will streamline the workflow from first principles theory into other fields of basic science and engineering projects that require a level of predictive power and an accuracy that the first principles construction of EOS can provide.

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