NASA Astrobiology Early Career Collaboration Award Report: A new multiphase water equation of state for astrobiology research

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An important part of studying the prospects for life and origins of life in ocean worlds is to develop an accurate equation of state (EOS) for water and aqueous mixtures. Thermodynamic properties computed from these EOSs serve as input to planetary evolution and simulation models, and the fidelity of these models often hinges on the accuracy of the EOSs that they employ. Despite broad scientific interest in water and its relevance to astrobiology, a reliable and accurate multiphase EOS for water that also covers high-pressure ice phases has not yet been developed. Professor J. Michael Brown and his research group at the University of Washington are well-recognized experts on the behavior of water at high-pressure conditions relevant to astrobiology. He and one of his postdocs, Dr. Baptiste Journaux, have developed a multiphase EOS for water that is applicable to the liquid phase [1], as well as to four solid phases: ices II, III, V, and VI [2]. They are currently working on extending their EOS to cover higher-pressure solids, including ices VII [3] and X. In particular, ice VII is thought to be the solid phase most relevant to large, oceanic exoplanets. By making their EOS applicable to the higher-pressure ices, one would obtain the first reliable, multiphase EOS that covers all the condensed phases of water relevant to astrobiology research. With funding from the collaboration award, I visited Professor Brown and Dr. Journaux for three weeks to help achieve this goal of extending their EOS to the higher-pressure ices.

The Brown and Journaux methodology involves expressing the EOS in terms of a free-energy model that they infer by integrating experimental data (e.g., those pertaining to the sound speed and the heat capacity) and theoretical predictions from *ab initio* quantum simulations (vibrational density of states). The free energy is not represented in terms of a single function that covers the entire pressure and temperature domain of interest, but instead by a series of splines that serve as a set of localized basis functions. An important step in their technique is to apply regularization to achieve smooth spline fits and help ensure that these fits satisfy known theoretical constraints. During my visit, I learned more about the mathematical details underlying their approach and ran their codes to produce the results illustrated in Figure 1. With perhaps some more refinement, the results from that figure, which represent the thermal contribution to the EOS, can be combined with recent room-temperature isotherm analyses from Brown and Journaux [4] to produce a complete EOS for high-pressure ices that can then be connected together with their earlier models on the liquid phase [1] and on the lower-pressure ices [2] to produce a multiphase water EOS that covers the entire range of pressure and temperature conditions relevant to astrobiology.

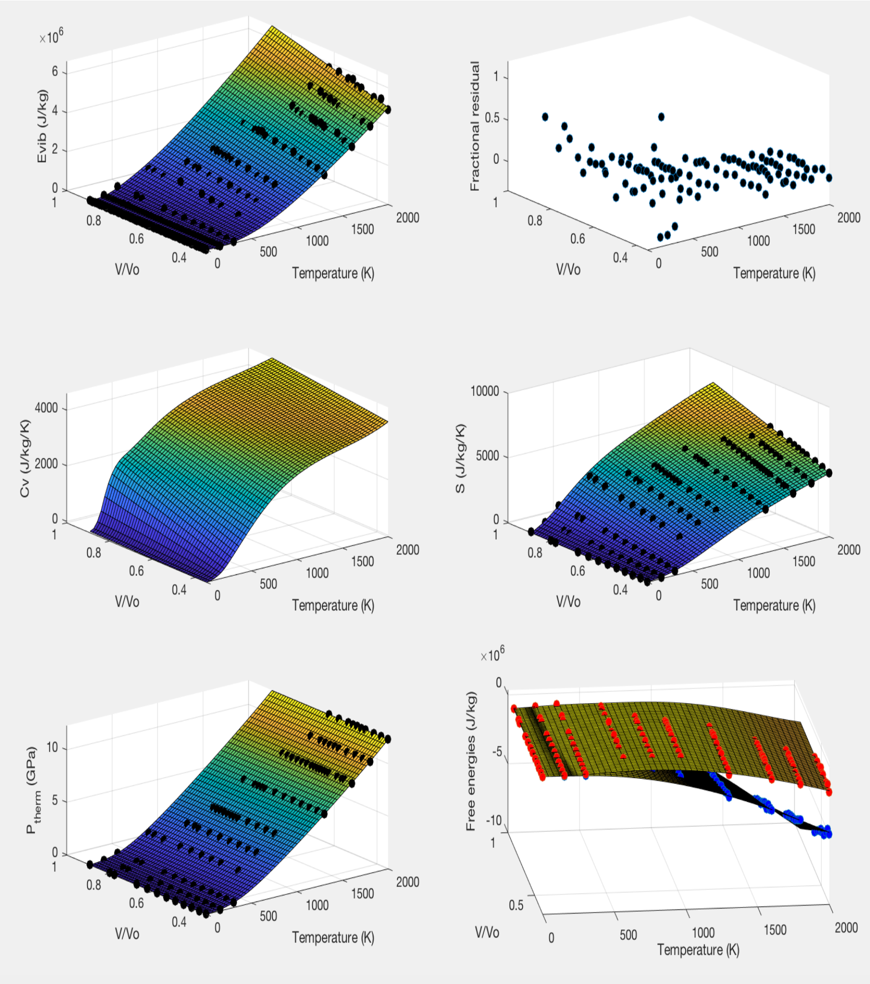

Figure 1: Results for the ion-thermal contribution (i.e., the contribution from motion of the nuclei) to the EOS obtained by applying spline fits and regularization to vibrational density-of-states results from *ab initio* quantum molecular dynamics (QMD) simulations performed by Hernandez [5]. The conditions shown here cover those relevant to the high-pressure ices VII and X, including metastable extensions. The volume axis is nondimensionalized in terms of the compression ratio, where V_0 is a chosen reference volume. Proceeding clockwise from the uppermost-left figure, the individual panels illustrate the ion-thermal contribution to the internal energy, the fractional residual of the difference between the spline fit and the QMD results for the internal energy, the entropy, the ion-thermal contributions to the Gibbs energy (upper surface cutting through the red points) and Helmholtz energy (lower surface cutting through the blue points), the thermal pressure, and the heat capacity. Note that by design the splines do not produce an exact fit to the QMD results (the residuals in the uppermost-right figure are not all zero) because we have applied regularization so that we have smooth free-energy surfaces with no discontinuities in the derivatives and so that our metastable extensions approach the theoretically correct asymptotic limits (e.g., heat capacity and entropy must be zero at 0 K). Also, we have assumed that the contribution to the EOS from electronic excitations is negligible for the conditions we have examined.

This collaboration has led to a number of other favorable outcomes. First of all, the EOS-development methodology of Brown and Journaux could greatly benefit the ongoing work at LLNL. A major thrust of my research and that of several of my LLNL colleagues is to develop equations of state for various materials that cover a very wide range of pressures and temperatures. Using splines (i.e., localized basis functions) more extensively in our EOS formalism, along with techniques like regularization, could help improve the fidelity and robustness of the LLNL equations of state, as well as make our EOS-development process more automated and less cumbersome. Towards this goal, we will mentor a graduate student from the Brown group for an internship in the coming summer to implement and adapt some of their ideas to our work. The multiphase water EOS will have a tangible effect on NASA missions by feeding into planetary evolution models at JPL [6] and other key institutions. A natural followup to this work is to extend this pure water EOS so that it can also handle aqueous mixtures, which could be the subject of future collaborations between LLNL, JPL, and the University of Washington. One possibility is to develop an EOS for water–CO_2 mixtures, and this could involve a recent, high-pressure CO_2 EOS produced at LLNL [7]. I gratefully acknowledge funding support from the NASA Astrobiology Institute for this excellent opportunity and again thank Professor Brown and Dr. Journaux for a productive, exciting collaboration. I would also like to thank two additional people: Dr. Steve Vance at JPL for his support for this collaboration and hosting my earlier visit to JPL; and Dr. Jean-Alexis Hernandez at the University of Oslo for providing the QMD data used to construct the results shown in Figure 1.

References

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