Proposal for Young Scientist IAPWS Fellowship Project

Towards an IAPWS Guideline for the Thermodynamic Properties of Supercooled Water

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Young Scientist

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Abstract

Support is requested for an IAPWS Fellowship for a young scientist, Vincent Holten, to pursue research "Towards an IAPWS guideline for the thermodynamic properties of supercooled water"

1. INTRODUCTION

During the past decades considerable amount of experimental information for thermodynamic properties of supercooled water has become available (see Attachments). These experiments have revealed an anomalous temperature dependence of the isobaric heat capacity, the isothermal compressibility, and the thermal expansivity coefficient of supercooled water. Several scenarios for explaining the anomalous behavior of these thermodynamic properties have been proposed. One theoretical possibility is the suggested presence of a metastable liquid-liquid critical point in supercooled water.

In a previous project supported by IAWPS it was demonstrated that a simple engineering-type cubic mean-field equation of state did indicate that the presumed existence of such a liquid-liquid critical point does yield a plausible physical explanation of the anomalous temperature dependence of the thermodynamic properties mentioned above (Attachment I). This observation was confirmed by Bertrand and Anisimov [1] on the basis of a nonclassical model for the critical thermodynamic behavior of supercooled water. The analysis of Bertrand and Anisimov [1], as well as some earlier work of Fuentevilla and Anisimov [2], encouraged us to embark on a project towards the possible development of a theoretical model for the thermodynamic properties of supercooled water that would yield not only a physical explanation for the anomalous temperature dependence of heat capacity, compressibility, and expansivity, but also an accurate representation of all experimental data, include the dependence of volume or density on temperature and pressure. A report on the status of this project is presented in Appendix II.

The project proposed will not only enable IAPWS to be actively engaged in a subject of considerable contemporary scientific interest , but it is also of direct relevance to IAPWS, since the thermodynamic behavior of supercooled water serves as a reference standard for a description of the thermodynamic properties of seawater. For future work of IAPWS on the thermodynamic properties of seawater information for the equation of state of supercooled water at least down to –25°C and up to 150 MPa will be desirable [3]. As documented in Attachment II, extrapolation of the IAPWS-95 formulation for the thermodynamic properties of H_2O does not yield a satisfactory representation of the thermodynamic properties of supercooled water.

2. Issues

In Attachment II it is demonstrated that a theoretical model based on the existence of a metastable liquid-liquid critical point can represent the experimental thermodynamic property data of supercooled water up to pressures of 150 MPa, which is the pressure range of direct interest to IAPWS [3]. It is even possible to modify the model empirically so as to obtain a representation of the thermodynamic properties of supercooled water up to pressures of 400 MPa. However, before we can propose a guideline for a fundamental equation of state for supercooled water, still a number of issues need to be addressed.

First the theoretical model assumes a linear dependence of the liquid-liquid curve on temperature and pressure. While the location of this liquid-liquid curve is somewhat uncertain, it is likely not a straight line as a function of temperature and pressure. We need to investigate how to incorporate curvature of the liquid-liquid transition line into the theory.

The presumed existence of a liquid-liquid critical point is not the only possible explanation proposed for the anomalous behavior of the thermodynamic properties of supercooled water as discussed in Section 7 of Attachment II. A scientifically extremely interesting question is whether we can rule out any of the other scenarios suggested for the cause of the anomalous thermodynamic behavior of supercooled water. One example to be addressed is whether response functions, like the compressibility, diverge at only one temperature corresponding to a critical temperature, or to a range of temperatures corresponding to a spinodal curve.

Nevertheless, without prejudging the results of the results, we do think it should be possible to develop a reliable guideline for the thermodynamic properties of supercooled water al least in the range of temperatures and pressures of direct relevance to an IAPWS.

Another goal of the project is the development of a representative equation for the surface tension of supercooled water. The research will be pursued in collaboration with the Institute of Thermodynamics, Academy of Sciences of the Czech Republic, where scientists have embarked on an experimental program for measuring the surface tension and of densities at high pressures of supercooled water.

3. Young investigator

We have found a young scientist, Vincent Holten, from the Technical University Eindhoven who is uniquely qualified to pursue this research. A Curriculum Vitae of Vincent Holten is presented in Attachment III.

Vincent Holten has a Ph.D. from the Technical University Eindhoven in The Netherlands. As part of his Ph.D. research he studied the thermophysical properties of supercooled water and his thesis contains a review of this subject. In Eindhoven he also started collaboration with Jan Hrubý on the surface tension of supercooled water.

From April 1, 2011 till the present Vincent Holten has been working as a Visiting Assistant Research Scholar at the University of Maryland on the subject of thermodynamic modeling of supercooled water. The stay of Vincent Holten at the University of Maryland was part of an exchange program between the Burgers Program for Fluid Dynamics at the University of Maryland and the J.M. Burgerscentrum for Fluid Mechanics in The Netherlands. Vincent Holten is also the leading author of Attachment II.

3. Implementation of project

We envision a nine-month project starting October 1, 2011. For this purpose Vincent Holten will return to the University of Maryland the end of September on a travel grant from the J.M. Burgerscentrum in The Netherlands. His stay at the University of Maryland from October 1 till December 31, 2011 will be supported by a research grant from the Division of Chemistry of the US National Science Foundation. We request IAPWS support for a six-months stay of Vincent Holten at the University of Maryland from January 1 till June 30, 2012. A report on the research to be completed under this project will be reported at the 2012 annual meeting of IAPWS.

3. Budget (in $ US)

Subsistence for 6 months for IAPWS Young Scientist……$ 19,200

References

[1] C.E. Bertrand and M.A. Anisimov, J. Phys. Chem. B, in press.
(doi: 10.1021/jp204011z).
[2] D.A. Fuentevilla and M.A. Anisimov, Phys. Rev. Lett. **97**, 195702 (2006), erratum ibid. **98**, 149904 (2007).
[3] R. Feistel, private communication (2011).

Attachment I: J. Kalova, R. Mareš, M.A. Anisimov, and J.V. Sengers, *Scaled equation of state for supercooled water in the mean-field approximation*, Technical Report (International Association for the Properties of Water and Steam, September, 2011).

Attachment II: V. Holten, C.E. Bertrand, M.A. Anisimov, and J.V. Sengers, *Thermodynamic modeling of supercooled water*, Technical Report (International Association for the Properties of Water and Steam, September, 2011).

Attachment III: Curriculum Vitae of Vincent Holten

Note: This proposal has been endorsed by Andre Zeijseink, representative of IAPWS in The Netherlands.