Young Scientist IAPWS Fellowship Project

Thermophysical Properties of Supercooled Water

IAPWS Sponsors

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Young Scientist

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1. BACKGROUND

The anomalous enhancements of isothermal compressibility, isobaric heat capacity, and in the magnitude of the thermal expansion coefficient of liquid water upon supercooling have been interpreted in terms of a retracing spinodal curve [1, 2], in terms of singularity free interpretation of the thermodynamics of supercooled water [3], and in terms of the metastable, low-temperature critical point. The second-critical-point scenario [4] is leading theory now. Recent experiments have given an indirect support for this liquid-liquid critical point [5].
Liquid water can be supercooled to -41 °C at atmospheric pressure and -92 °C at 2.10^8 Pa. These limits are the boundary where experimental data exist. The temperature T_H is called homogenous nucleation temperature. If water is rapidly cooled below T_H, water freezes into glassy, amorphous solid, forming at low pressure a low-density amorphous state (LDA) and at high pressure a high-density amorphous state (HDA). For LDA and HDA states there are estimations of thermophysical properties of water [6]. Experimental data for bulk water are missing for temperatures between150 K and 232 K.
Recently, Fuentevilla and Anisimov [7] have published a scaled parametric equation of state that is universal in terms of theoretical variables and belongs to the three-dimensional Ising-model class of universality. The equation can be used to describe and predict properties of supercooled water. The main advantage of the scaled equation mentioned above is the possibility to predict some properties of supercooled water below the limit of homogenous nucleation, for which it is very difficult to obtain experimental data.
Kalova and Mares [8] used the theory to predict vapour pressure of supercooled water for calculation of correction terms to Wagner and Pruß [9] equation. The extrapolation based on the theory extends temperature interval of validity below 0 °C to - 150 °C.
Fuentevilla and Anisimov equation [7] uses several parameters, e.g. location of the second critical point and coefficients of the equation. The coefficients are calculated from the liquid – liquid coexistence curve and from Widom line. The experimental heat-capacity data [10] are used for estimation of the second critical point parameters. The scaled equation is valid only in the immediate vicinity of the critical point, but available experimental data are far away from it. Analytical background functions are needed to describe thermophysical properties in a larger distance from the critical point.

2. SCOPE

The calculation of properties using existing experimental data or data calculated from IAPWS 95 brings quite complex analytical background function in some cases (Kalova, Mares [11]). It is the reason to calculate all coefficients of the scaled equation including parameters of the second critical point again. It is possible to use not only experimental data and estimations from the range of amorphous ice but also data from IAPWS 95 for the calculation. The extrapolation of properties gained from IAPWS 95 can be tested on a model.
Planned steps:
- Overview and critical evaluation of existing experimental data for supercooled water, not only at ambient pressure, and critical evaluation.
- Analysis of Widom line (experimental limits of stability, computer simulations).

- Experimental data on amorphous ice can be used to constrain the thermodynamics functions of water at temperatures below 155 K.
- Extrapolation of IAPWS 95 and other formulations of properties in the supercooled temperature range.
- Recalculation of coefficients in the scaled equation including the second critical point parameters.
- Finding the background functions for specific thermophysical properties of water.
- Evaluation of the scaled equation and comparison with IAPWS 95 and with experimental data.

3. PROPOSED RESEARCH AND JUSTIFICATION FOR IAPWS SUPPORT

The purpose of the collaborative project with IAPWS is to recalculate coefficients in the scaled equation and to compare gained thermophysical properties with extrapolated values from IAPWS 95. The IAPWS funding will make it possible to spend at the University of Maryland for six months in a single stay starting in January 2010.

4. BUDGET (in $US)

Total Cost...$18000
Subsistence for 6 months: IAPWS Young Scientist Grant..................$15000
Travel (round trip): to be paid by Institute of Technology and Business
in Ceske Budejovice...$3000

5. BIBLIOGRAPHY

[1] R.J.Speedy, Stability-Limit Conjecture. An Interpretation of the Properties of Water, J.Phys.Chem. 86:982 (1982)
[2] R.J.Speedy, Limiting Forms of the Thermodynamic Divergences at the Conjectured Stability Limits in Superheated and Supercooled Water, J.Phys.Chem. 86:3002 (1982)
[3] S.Sastry, P.G.Debenedetti, F.Sciortino, H.E.Stanley, Singularity-free interpretation of the thermodynamics of supercooled water, Phys.Rev.E 53: 6144 (1996)
[4] O.Mishima, H.E.Stanley, The relationship between liquid, supercooled and glassy water, Nature 396, 329-335 (1998)
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[6] F. W. Starr, C. A. Angell, H. E. Stanley: Prediction of entropy and dynamic properties of water below the homogeneous nucleation temperature, Physica A 323: 51-66 (2003)
[7] D. A. Fuentevilla, M. A. Anisimov: Scaled Equation of State for Supercooled Water Near the Liquid-Liquid Critical Point, Phys. Rev. Lett. 97: 195702 (2006)
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[9] W. Wagner and A.Pruß: International equations for the saturation properties of ordinary water substance: Revised according to the international temperature scale (1990). Addendum to J. Phys. Chem. Ref. Data 16: 893 (1987), J. Phys. Chem. Ref. Data 22:
783-787

[10] C. A. Angell, M. Oguni, W. J. Sichina: Heat capacity of water at extremes of supercooling and superheating, J. Phys. Chem. 86: 998-1002 (1982)
[11] J. Kalova, R. Mares: Scaled Equation of State for Supercooled Water - Comparison with Experimental Data and IAPWS 95, Proceedings of the 15th International Conference on the Properties Water and Steam, Berlin/Germany, September 7-11 (2008)

6. CURRICULUM VITAE

Jana Kalova

Born

1965

Education

2007- University of West Bohemia, Faculty of Mechanical Engineering, Pilsen, Czech Republic, PhD. stud., programme Thermomechanics and Fluid Mechanics
2007 University of West Bohemia, Faculty of Applied Science, Pilsen, Czech Republic, RNDr.
2003-2006 University of West Bohemia, Faculty of Applied Science, programme Mathematical engineering – Mathematical modelling, Pilsen, Czech Republic, Ing.
1985-1989 University of South Bohemia, Pedagogical Faculty, programme Mathematics and Physics, Ceske Budejovice, Czech Republic, Mgr.

Employment

2007- Assistant Profesor, Institute of Technology and Business in Ceske Budejovice
1994 - 2007 High-school teacher of mathematics, in Ceske Budejovice

IAPWS WG PCC

07 September 2009

Proposal for IAPWS to support International Collaboration Project

IMPROVED SAMPLING TECHNIQUES

Participants

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Young Scientist/Student

TBD – from Japan.

Background

The formation and transport of corrosion products in water/steam cycles has been a major problem since the inception of thermal energy circuits. The determination of corrosion product concentrations has subsequently become a very important method of monitoring the chemical state of an operating unit. Since the solubility of the corrosion products is rather low at the conditions of the water/steam cycle, they appear mainly as particulates. This complicates the sampling, as the heterogeneous character of the system can easily lead to partial separation of phases resulting in non-representative sampling. This problem becomes particularly pronounced at low concentrations of corrosion products.

A previous IAPWS-sponsored International Collaboration considered sampling effectiveness in high-temperature systems from the point of view of the design of sampling nozzles and the importance of imposing isokinetic conditions. A commercial computational fluid dynamics code was used to model the sampling efficiency for micrometre-sized particles of corrosion products in steam and water. It was concluded that imposing isokinetic conditions is inconsequential in water systems, since the apparent concentration of particles taken into a nozzle is virtually unaffected by the sampling velocity. In steam systems, however, practical nozzles always perturb the fluid flow field and lead to apparent concentrations of particles that deviate from the true concentrations. The deviations depend on sampling velocity as well as particle size [1,2,3].

While the collaboration successfully identified issues with sampling nozzles, it was clear that interactions between the sample drawn into the nozzle and the walls of the sample line (including the cooler) may well dominate and be the major cause of unrepresentative results. It was concluded that there is a need to study the interactions with a view to minimising them and proposing methods of correcting for them.

Objective

The objective of this project is to assemble relevant information from the literature and identify the best practices for current sample systems to minimise sample-wall interactions. This will lead to the design of a program of laboratory research in a high-temperature water system that would lead to an understanding of the mechanisms involved so that optimal sample systems can be designed in the future and a capability for predicting and correcting for interactions can be obtained.

Completion

The student will spend a year in Derek Lister's laboratory at the University of New Brunswick in Canada. There, she/he will interact with staff who have already been involved with the previous IAPWS International Collaboration on sampling. He/she will become familiar with the operation of high-temperature water systems and how they are sampled. Preliminary experiments on evaluating the sample systems will be performed and the results will help in the formulation of a detailed research program for the future.

Deliverables

Report on "Effect on Quality of Samples from High-Temperature Systems of Interaction with Sample System Materials".

Schedule

The work will be done in 2010 and the report delivered at the IAPWS meeting in 2011.

Budget

Item	**Cost ($US)**	
Student travel cost	3 000	
Student cost of living	16 000	
Materials and supplies	2,500	
Local costs	1 500	
Time of participants	20 000	
Total	**43 000**	
Cost to IAPWS	**12 000**	

Requested contribution from IAPWS is $ 12 000.

References

1 P. Srisukvatananan, D.H. Lister, R. Svoboda, K. Daucik. "Assessment of the state of the art of sampling of corrosion products from water / steam cycles". Power Plant Chemistry 10 (2007) 10, pg 613-626

2 P. Srisukvatananan, D.H. Lister, Chien-Ee Ng, R. Svoboda, K. Daucik. "Corrosion Product Sampling in Power Plants under Water/Steam Cycle Conditions". 15th International Conference on the Properties of Water and Steam, Berlin / DE, Sep 8 - 11, 2008. Power Plant Chemistry, 10 (2008) 10, pg 575-585

3 P. Srisukvatananan, D.H. Lister, R. Svoboda, K. Daucik. " A CFD Study of Corrosion Product Collection Efficiency of Sampling Nozzles under Power Plant Conditions". 9th International EPRI Conference on Cycle Chemistry in Fossil and Combined Cycle Plants with Heat Recovery Steam Generators, June, Boston / USA