

# Oponentní posudek disertační práce

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Název disertační práce:	Thermodynamic modeling of supercooled water
Vedoucí disertační práce:	prof. Ing. Radim Mareš, CSc.
Vysoká škola:	Západočeská univerzita v Plzni, Fakulta strojní
Oponent:	Ing. Jan Hrubý, CSc., Ústav termomechaniky AV ČR, v.v.i.

V předložené disertační práci "Termodynamické modelování podchlazené vody" popisuje RNDr. Ing. Jana Kalová (dále disertantka) nový pohled na termodynamické modelování podchlazené vody. Navržené matematické modely vystihují chování všech termodynamických vlastností podchlazené vody, zejména známých anomálií, na základě hypotézy tzv. druhého kritického bodu. Disertační práce je výsledkem samostatné práce disertantky pod vedením prof. Mareše a ve spolupráci s University of Maryland, kde disertantka pracovala v rámci výzkumné stáže sponzorované Mezinárodní asociací pro vlastnosti vody a vodní páry (IAPWS) a Ministerstvem školství, mládeže a tělovýchovy ČR.

Disertační práce obsahuje velmi důležité výsledky v oboru termofyzikálních vlastností tekutin. Vlastnosti podchlazené vody jsou zajímavé nejen samy o sobě jako předmět akademického výzkumu, ale také pro důležité aplikace v letectví, meteorologii, kryobiologii. Předmětem disertační práce je vytvoření termodynamických modelů na základě platných teoretických předpokladů. Parametry těchto modelů jsou určeny na základě existujících experimentálních dat. Pomocí navržených modelů je možné nejen reprodukovat hodnoty odpovídající měřeným hodnotám, ale také určit hodnoty veličin přímo neměřených – např. tlak syté páry podchlazené vody.

Přiměřená obecná rešerše o vlastnostech metastabilních kapalin a speciálně podchlazené vody je obsahem 1. kapitoly. Další odkazy na literaturu jsou uvedeny v dalších kapitolách. Celkem obsahuje seznam literatury přes 100 položek a vytváří komplexní obraz o současném stavu poznání v oboru. V 2. kapitole podává disertantka obecný výklad teorie kritického bodu a upřesňuje svůj model definicí teplotní závislosti parametrů Landauovy teorie (k tomu se vztahuje jedna otázka k oponentuře) a popisuje výsledky Isingova modelu, které jsou přijímány jako univerzálně platné pro kritické jevy v tekutinách. V 3. kapitole uvádí svůj model parametrické stavové rovnice založený na škálovací teorii. Zajímavý je test různých souborů kritických exponentů a jejich vliv na linearitu funkce  $M(\theta)$ , udávající „úhlovou“ závislost parametru uspořádání. Výsledky testu, uvedené na obrázku 3.1 ukazují, že pro nejméně pravděpodobnější soubor exponentů je tato funkce vskutku velmi blízká lineární závislosti. Další podrobnosti škálovací teorie jsou uvedeny ve 4. kapitole, kde je zejména specifikována škálovací stavová rovnice podchlazené vody. V kapitole 5. je použita přechodová (crossover) stavová rovnice pro výpočet tlaku syté páry podchlazené vody. Významným výsledkem této části je rovnice (5.3.1) umožňující výpočet tohoto tlaku v širokém rozmezí teplot. K této problematice se váže jedna z otázek k oponentuře. V kapitole 6. je zpracována problematika povrchového napětí podchlazené vody. Zejména je studována otázka druhého inflexního bodu teplotní závislosti povrchového napětí. Jsou navrženy dvě varianty upravené rovnice. K tomu se váže jedna z otázek k obhajobě. V kapitole 7. jsou

zpracovány poslední výdobytky termodynamického modelování podchlazené vody dosažené v rámci spolupráce disertantky s pracovníky University of Maryland. V kapitole 8. je popsán zjednodušený termodynamický model, založený na přiblížení středního pole (mean field approximation). Je zajímavé, že tento model reprodukuje měřená data v rámci jejich experimentálních nejistot. Zejména je zajímavá diskuse nejistot odhadu polohy druhého kritického bodu. Nejistoty tohoto odhadu jsou závislé, jak ukazuje obrázek 8.6. Kapitola 9. uvádí závěry disertační práce.

Celkem lze konstatovat, že použité metody a postupy vývoje termodynamických modelů a jejich testování byly správné a zajímavé.

Prosím disertantku, aby při obhajobě uvážila odpovědi na tyto otázky:

1. V kapitole 2. je uvedena Landauova teorie fázového přechodu druhého řádu. Jak se tato teorie aplikuje na kritické jevy v tekutinách – včetně předpokládaného druhého kritického bodu v podchlazené vodě, když tyto fázové přechody jsou prvního řádu?

2. Pro výpočet tlaku syté podchlazené vody byla použita dvojitá integrace rovnice (5.1.1) a (5.1.2). Nejvýznamějším přínosem zde je využití přechodové stavové rovnice. Nicméně jako jeden vstup byla použita rovnice pro isobarickou tepelnou kapacitu vody ve stavu ideálního plynu (5.1.4), převzatá z literatury. Proč pro tento výpočet nebyla použita formulace IAPWS-95, která udává přesnou isobarickou tepelnou kapacitu ideálního plynu až do teploty 130 K, popřípadě její nedávno publikované zobecnění do teploty 50 K? Dvojitý integrál by nebylo nutné počítat, jedná se totiž v podstatě o výpočet Gibbsovy energie, která je v IAPWS-95 implementována.

3. Experimentální data a data z molekulárních simulací pro povrchové napětí stabilní a podchlazené vody byla korelována dvěma rovnicemi ve společném tvaru (6.2.5), lišícím se hodnotami koeficientů a exponentů. V první variantě byl optimalizován jen doplňující člen, pro který byl nalezen exponent  $n=3$ . Při optimalizaci i původní části byl určen vysoký exponent  $n=33$ . V praxi je třeba počítat povrchové napětí i při teplotách kolem 200 K. Extrapolace obou rovnic potom dá zřetelně odlišné výsledky a varianta s vysokým exponentem bude patrně vzdálená fyzikální realitě. Můžete provést porovnání extrapolací chování těchto rovnic a popřípadě je porovnat s jinými rovnicemi, navrženými pro tento extrémní teplotní interval?

Cíle disertace jsou uvedeny v jejím úvodu:

A. testovat možnosti popisu experimentálních dat pro podchlazenou vodu pomocí úplného škálování a pomocí aproximace středního pole (mean-field approximation),

B. analyzovat experimentální data pro povrchové napětí a testovat možnost existence druhého inflexního bodu teplotní závislosti povrchového napětí.

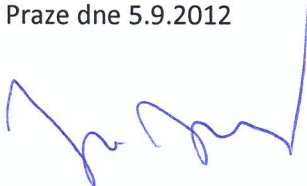
Z výše uvedeného rozboru vyplývá, že tyto cíle byly v disertační práci splněny.

Práce je uspořádána pro čtenáře přehledně, poněkud nesystematicky působí střídání pasáží řešeršního charakteru s pasážemi obsahujícími tvůrčí přínos disertantky. Z obsahu je ale tvůrčí přínos zřejmý. Formální úprava práce je dobrá, jen obrázky by mohly mít lepší kvalitu, která je zřejmě omezena programem, který disertantka používá k tvorbě grafů. Práce je psána dobrou angličtinou.

Části disertace zpracovala disertantka do úctyhodné řady publikací. Publikace o výpočtu tenze par podchlazené vody v impaktovaném periodiku International Journal of Thermophysics už vyšla, další dvě jsou předloženy do stejného časopisu. Disertantka hojně publikovala také v tuzemských periodících a na konferencích, celkem dosahuje soupis jejích publikací čísla 20.

Na základě výše uvedených skutečností **doporučuji** disertační práci k obhajobě podle zákona č. 111/1998 Sb. § 47.

V Praze dne 5.9.2012



Jan Hrubý

# Examiner's Report of Ph.D. Thesis: "Thermodynamic Modeling of Supercooled Water"

by RNDR. Ing. Jana Kalová  
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Faculty of Mechanical Engineering

May 16, 2012

## **1 Overall Evaluation and Referee's Decision**

My evaluation follows the "Instructions for elaboration of the examiner's report" of Západočeská univerzita v Plzni, děkanát Fakulty strojní, Plzeň as well as commonly accepted and recommended rules for publications in journals addressing subjects of atmospheric chemistry and physics.

1. The PhD thesis addresses relevant scientific questions of interest within the scope of thermomechanics, fluid mechanics, as well as atmospheric chemistry and physics.
2. The study presents novel methodical concepts, ideas, and thermophysical data.
3. The author reached substantial conclusions.
4. The scientific methods and assumptions are valid and, overall, clearly outlined. The approach is very interesting, challenging, and very elegant. Some parts, however, could have been presented with more details (see my specific comments).
5. The results are sufficient to support the interpretations and conclusions.

6. The description of the approach and calculations is sufficiently complete and precise, and allows their reproduction by fellow scientists (traceability of results). However, the derivation of the scaling law from the 3D Ising model seems to be a very tricky matter, which cannot be solved *en passant*. This task is very challenging and requires theoretical work at the roots. I could imagine that “on foot” rederivation of the fundamental and beautiful scaling relation given by Eq. (2.2.1) would evoke a feeling of deep satisfaction and sense of delight.
7. The author gives proper credit to related work and clearly indicates her own new/original contribution. In this context I would like to emphasise the formidable publication list of the author and her close and very fruitful co-operation with the theoretical schools of Professor Mikhail A. Anisimov and Professor Jan V. Sengers.
8. The title clearly reflects the contents of the PhD thesis.
9. The abstract provides a concise and complete summary.
10. The overall presentation is well structured and clear.
11. The language is fluent and precise. I have enjoyed to read the PhD thesis.
12. The mathematical formulae, symbols, abbreviations, and units are correctly defined and used. There are some typos in the document, which, however, do not affect the evaluation of the study (see specific comments).
13. The number and quality of references are appropriate.

As one of the most important points of this study I want to emphasise the enormous gain of new insights and practically useful results at a minimum of technical and infrastructural investment. It is very instructive to see what can be extracted from already available, but quality assured data if one has an intelligent plan. This is exemplary (because it is not a matter of course)! At this, the role of theoretical predictions like the present one is remindful of the following plea by J. Willard Gibbs: “*It is the office of theoretical investigation to give the form in which results of experiments may be expressed.*”.

**I recommend the doctoral thesis for defence.**

## 2 Supplement: Explanatory Statements

### 2.1 Relevance of the Study

The PhD thesis addresses an important question of geophysical interest, namely the determination of thermophysical properties of supercooled water. This subject is not only of theoretical interest but also of high practical relevance. In the atmospheric community, e. g., it is commonly accepted that the uncertainties in state-of-the-art numerical weather prediction and climate models are mainly caused by an insufficient treatment of cloud processes. This, in turn, is to a large extent related to our limited understanding of atmospheric aerosol, hydrosol, and hydrometeor formation via vapour  $\rightleftharpoons$  liquid  $\rightleftharpoons$  solid phase transitions and subsequent microphysical processes in turbulent media. Atmospheric ice formation and the physical characterisation of supercooled water play an outstanding role among these processes. Both represent “hot spots” of current research in atmospheric chemistry and physics.

The overcoming of present days shortcomings in description of atmospheric ice formation requires (a) more advanced theoretical approaches, (b) sophisticated field and laboratory experiments to elucidate the process phenomenology and to restrict theories, and last but not least (c) combined theoretical and experimental approaches to consolidate the input parameter database for cloud modelling, i. e., the determination of the required thermophysical (thermodynamic and non-thermodynamic) parameters of supercooled water and ice. The present study provides an important contribution to these three points, especially to point (c).

The properties of supercooled water in the so-called “no man’s land” (cf. Figure 1.1) are of special importance for tropospheric Cirrus clouds formed at  $H=8-12$  km at temperatures down to  $-80^{\circ}\text{C}$  in the equator region, for Polar Stratospheric Clouds formed at  $H=15-25$  km at temperatures below  $-78^{\circ}\text{C}$ , and for Noctilucent Clouds (or Polar Mesospheric Clouds) formed at  $H=80-100$  km at temperatures below  $-120^{\circ}\text{C}$ .

Frank’s *bon mot* (1972) “Of all known liquids, water is probably the most studied and least understood” owes its actuality to a large extent to our insufficient understanding of metastable water. In this context “no man’s land” of supercooled water is both a well defined physical notion and a scientific program.

## 2.2 Review of the Scientific Content of the Study

The present section includes a detailed description of my perception of the present thesis. It has the character of an evaluation protocol and serves only for the substantiation of my conclusions, assessment, and specific comments listed later. **The subsequent items can be optionally jumped over.**

1. In **Chapter 1** the author gave a brief and meaningful characterisation of metastable liquids including the thermodynamic and kinetic limits of liquid water and available experimental data of thermodynamic properties from the literature. Then, different physical theories for the explanation of the metastable behaviour of liquids were briefly characterised. **Chapter 1 gives a good introduction into the problem of interest.**
2. In **Chapter 2** the author discussed the two main theoretical approaches to describe the metastable behaviour of water. Starting point here is the employed hypothesis of the existence of a liquid-liquid critical point (LLCP), which terminates the coexistence curve between a low-density and a high-density liquid phase:
  - Beyond the LLCP, the phase difference disappears and the fluid becomes homogeneous (bidirectional phase conversion without crossing the phase equilibrium line).
  - The phase transition at the critical point is a second-order phase transition according to the classical Ehrenfest classification: continuity of the zeroth and first derivatives of free energy, but discontinuity of its second derivatives (molar heat capacity, isothermal compressibility, thermal expansivity).

**Firstly**, in order to describe the second-order phase transition of metastable water, especially in the vicinity of the critical point, the author discussed the phenomenological Landau theory (a “mean field” theory), which is based on a Taylor expansion of the free energy in terms of an order parameter describing the symmetry of a phase (and the change of symmetry during a phase transition). At the critical point, the order parameter vanishes. **Secondly**, the author introduced into her approach the Ising model and focussed on a prediction obtained from the three-dimensional Ising model: the existence of a phenomenological, universal dependency between dependent ( $h_3$ ) and independent scaling fields (“strong” scaling field or ordering field  $h_1$ , and

“weak” or “thermal” scaling field  $h_2$ ) in the vicinity of the critical point (Eq. (2.2.1)). The scaling fields have a distinct physical meaning (near the critical point,  $h_1$  and  $h_2$  scale linearly with the physical fields). This relation is an equivalent form of the equation of state. At the critical point, this dependence has a singularity, hence  $h_3(h_1, h_2)$  cannot be analytically evaluated. **The existence of an universal relation  $h_3(h_1, h_2)$  is a very important result, its employment for the current purposes an excellent idea.**

3. In **Chapter 3** the author addressed the problem of evaluation of the universal scaling relation at the critical point. Owing to the impossibility to determine the dependent scaling field  $h_3$  at the critical point in an analytical way, the author followed an approach proposed by Schofield to parameterise the equation of state (“parametric equation of state”). **This approach is very tricky and interesting.** The independent variables  $h_1$  and  $h_2$  are transformed into the mathematically more convenient form of polar-like coordinates. This transformation leads, however, to the appearance of a new auxiliary universal analytic function ( $M(\theta)$  with  $\theta$  being one of the new coordinates, the angular parameter) in the calculus, which can be determined in a general way only from renormalisation-group theory of critical phenomena. In order to simplify the determination of  $M(\theta)$ , the author employed some approximations leading to the so-called “linear model” (Eq. (3.0.4)) and to the “cubic model” (Eq. (3.0.5)). In this form, the function  $h_3(h_1, h_2)$  can be determined numerically by solution of a transcendental equation. The author tested the validity of the “linear approximation” by use of different sets of universal critical exponents (from both experiments and theoretical studies) and found large deviations from the assumed linearity of the model (Fig. 3.1) in dependence of the employed set of critical exponents. In order to promote the use of the linear parametric equation of state, the author proposed a physically sound and traceable “readjustment” of model parameters. **The argumentation is physically sound, the evaluation of the presented calculus traceable by a fellow scientist.**
4. In **Chapter 4** the author evaluated different physical models for the relations between the (dependent and independent) scaling fields and physical fields (dimensionless forms of chemical potential, temperature, pressure).
  - **Firstly**, the “lattice gas model” was considered, which represents a model for the vapour–liquid critical point (Eq. (4.0.1)) with assumed



full vapour–liquid symmetry (“simple scaling”). It appears, that the employment of simple scaling leads to a “strongly fluctuating scaling density” or order parameter  $\phi_1$  (equal to the partial derivative of the dependent scaling field  $h_3$  with respect to the ordering field  $h_1$ , i. e.,  $\phi_1 = (\partial h_3 / \partial h_1)_{h_2}$ ), which is controlled solely by the density of the fluid (Eq. (4.1.2)).

- **Secondly**, based on symmetry arguments the thermal scaling field  $h_2$  of the lattice gas model was slightly modified (Eq. (4.1.8)) to consider some degree of asymmetry between vapour and liquid, which is typical for real fluids (“revised scaling”). In this case, the ordering field  $h_1$  becomes a function of both density and entropy of the fluid (Eq. (4.1.9)).
- **Thirdly**, the author discussed the case of a one-component fluid with consideration of full vapour–liquid asymmetry (“lattice liquid model”, “complete scaling”). In this model, the ordering and thermal scaling fields are postulated to be linear functions of chemical potential, temperature, and pressure. After mathematical rearrangement the author obtained thermodynamic relations establishing a link between physical and scaling densities (Eqs. (4.2.8), (4.2.9)). While the scaling fields were postulated to be linear combinations of the physical fields, the reverse functions of the physical fields were found to be non-linear combinations of the scaling fields. The author derived additional constraints on model parameters, which satisfy the thermodynamic conditions at the critical point (vanishing scaling fields). Therewith, final expressions for the dependencies of the scaling fields on physical fields were derived for complete scaling (Eq. (4.2.16)).
- **Fourthly**, the author evaluated a parametric equation of state for supercooled water recently proposed by Fuentevilla and Anisimov, according to which the ordering field  $h_1$  is a function of temperature (linear) and pressure (nonlinear), and the thermal scaling field  $h_2$  is a bilinear combination of temperature and pressure (Eqs. (4.3.1), (4.3.2)). The non-linear pressure term was introduced to correct for the curvature of the liquid-liquid transition (LLT) line. The condition  $h_1=0$  defines the Widom line (which is the continuation of the LLT line into the one-phase region; the Widom line corresponds to the locus of the maximum correlation length). The full model includes the governing equations for the strongly fluctuating (ordering) scaling density

$\phi_1 = (\partial h_3 / \partial h_1)_{h_2}$ , for the weakly fluctuating (thermal) scaling density  $\phi_2 = (\partial h_3 / \partial h_1)_{h_1}$ , as well as dimensionless isobaric heat capacity, isothermal compressibility, and thermal expansivity. In a similar way, the model of Mishima was presented.

**All these derivations and argumentation were physically sound to me.**

5. In **Chapter 5** the author evaluated the equation for the equilibrium vapour pressure of supercooled water for the determination of the molar isobaric heat capacity of metastable water. **I found this approach very interesting, tricky, and instructive.** Firstly, the author determined the molar isobaric heat capacity of water vapour,  $C_{p,\text{vap}}$ , from the paper of Murphy/Koop (2005). **At this, I have a specific comment on the determination of  $C_{p,\text{vap}}$  according to Eq. (5.1.4) (see below).** Therewith and with knowledge of the molar isobaric heat capacity of the liquid,  $C_{p,\text{liq}}$ , one can determine the molar latent heat of vaporisation. **Secondly**, the author employed three different ways to determine the very important molar isobaric heat capacity of the liquid,  $C_{p,\text{liq}}$ :

- **path 1:** approximative determination of  $C_{p,\text{liq}} \approx C_{p,\text{ice}} + 2 \text{ J mol}^{-1} \text{ K}^{-1}$  using the  $C_{p,\text{ice}}$  parameterisation of Murphy/Koop (2005, Eq. (4)) (see Eq. (5.1.5));
- **path 2:** integration of the Fuentevilla–Anisimov scaled equation of state of supercooled water (Eqs. (4.3.6), (5.2.1)) with physically reasonable assumptions outlined on pp. 41-42 [items A) to F)];
- **path 3:** determination of  $C_{p,\text{liq}}$  from evaluation of the Clausius–Clapeyron equation according to Eqs. (5.1.1), (5.2.3) with employment of  $C_{p,\text{vap}}$  from Eq. (5.1.4) and the equilibrium water vapour pressure over supercooled water according to Murphy/Koop (2005, Eq. (10)) (see Eqs. (5.0.2)).

**This approach follows a very good and yielding idea! The result depicted in Fig. 5.4 is physically plausible, very interesting, and of high relevance (see specific comment on Fig. 5.4 below).**

6. In **Chapter 6** the author investigated the temperature dependence of the surface tension of supercooled water,  $\sigma$ . One challenge here was the identification of the so-called “second” inflection point in the temperature dependence of  $\sigma$ . Starting point of the analysis is the IAPWS prediction of

$\sigma$  in the temperature range from the triple point to the critical temperature (Eq. (6.1.1)). Using evaluated data gained in the IAPWS Release on the Surface Tension of Ordinary Water Substance (1994), the author recalculated the coefficients of the IAPWS equation (6.1.1) to ensure a better fit (Tab. 6.1). From the revised expression (the same formula but with revised parameters) the first inflection point was derived ( $T_i=529.1$  K). In order to proof the existence of a second inflection point, the author tried to extent her  $\sigma(T)$  data series by consideration of experimental data for supercooled water from different sources (Fig. 6.3). However, owing to the lack of information required to ensure compatibility of these data points with IAPWS surface tension data, the author decided to include alternatively surface properties obtained from molecular dynamics simulations by Lü/Wei (2006) in the temperature range from 228 K to 293 K. **It is very nice to see that MD data can be directly employed for the derivation of handsome parameterisations! Very good idea.** In order to find a unique expression for the surface tension, which is valid below and above the triple point, the author modified the IAPWS equation (6.1.1) by inclusion of an additional power term (Eq. (6.2.5)). By application of a physically sound and traceable multistep regression analysis the parameters of Eq. (6.2.5) were estimated. These parameters ensure the preservation of the IAPWS formulation for temperatures above the triple point. From the evaluation of the corrected parameterisation of the surface tension, the author concluded the existence of a second inflection point at 1.5°C (see Fig. 6.5). Finally, the author proposed a new correlation function for the surface tension of ordinary water between 228 K and 647 K. **Chapter 5 is traceable, the result given by Eq. (6.2.5) is directly applicable in cloud microphysical studies (see specific comment).**

7. In **Chapter 7** the author came up with a comprehensive review of most recent developments in modelling of supercooled water. The theoretical argumentation follows the same principles as in the previous chapters: (i) definition of the thermodynamic model, (ii) determination of the Widom line, (iii) derivation of governing equations for the determination of dimensionless thermodynamic properties, such as isothermal compressibility, isobaric thermal expansivity, and isobaric heat capacity. The author evaluated two models:

- the Bertrand–Anisimov model (see my specific comment to Fig. 7.1)

below),

- the Holten–Bertrand–Anisimov–Sengers (HBAS) model (the related peer-reviewed paper of Holten et al. in *Journal of Chemical Physics* (JCP) has been identified on the list of JCP Top 20 Most Read in March 2012!).

**This chapter has the character of a compilation study to evaluate results from other groups. It fits well into the structure and intention of the PhD thesis and is a valuable supplement.**

8. In **Chapter 8** the author described the Kalová–Mareš–Anisimov–Sengers (KMAS) model, which represents a mean field approximation of the scaled equation of state. Then, the author reported on her tests with this model during the research fellowship at the University of Maryland.

The employed thermodynamic model (Eqs. (8.1.1)-(8.1.3)) differs from the Bertrand–Anisimov model by specific points, which were clearly outlined. Similar to the Fuentevilla–Anisimov model in Eqs. (4.3.1), (4.3.2), the ordering field  $h_1$  was assumed to be a linear function of dimensionless temperature and a nonlinear function of dimensionless pressure, and the thermal scaling field  $h_2$  to be a bilinear function of pressure and temperature. The neglect of contributions from chemical potentials to the scaling fields was justified with the restriction of the relevance of chemical potentials to highly asymmetric systems only (see my specific comments on the notion “symmetry”). The author proposed some modifications (such as reformulation of the scaling functions in terms of physical potentials rather than in physical pressure) to obtain simpler expressions for some thermodynamic properties. Then, the author evaluated the obtained expressions for the classical limit (“mean-field approximation”) by a special choice of the critical exponents (see Tab. 2.2,  $\alpha=0$ ,  $\beta=1/2$ ). The application of the KMAS model (as all other models based on Eq. (2.2.1)) is restricted to the determination of the “critical contributions” to the different thermodynamic parameters. For the background (noncritical) contributions, empirical temperature dependent functions have been proposed (Eqs. (8.1.19)-(8.1.21)). **For the isobaric heat capacity, depicted in Figs. 8.1, 8.2, holds what I wrote in the specific comments for other model predictions: it should be part of a comprehensive intercomparison study in the future and be applied to the determination of the melting enthalpy in the “no man’s land” of supercooled water.**

In Subsection 8.2, the author presented most recent results in research of the mean-field approximation, among them her own studies. An advantage of the mean-field approximation is its simplicity and suitability for practical applications. In order to extend the application of the scaling relation given by Eq. (2.2.1) from the local regime of “asymptotic behaviour near the LLCP” to the global regime of physical fields (complete representation of the thermodynamic properties), a regular, analytic background contribution of the dimensionless chemical potential has been added (Eq. (8.2.3)). This background contribution is represented by a truncated Taylor-series expansion around the critical point (Eq. (8.2.4)). After sound assumptions and rearrangement, the author arrived at analytical expressions for the dimensionless isothermal compressibility, the expansivity coefficient, and the isobaric heat capacity of metastable water. **By means of the cited literature, these calculations are traceable.** To overcome the singularity problem at the critical point, the earlier in the PhD thesis introduced transformation of the physical variables into polar-like coordinates was employed. Then, the mean-field approximation ( $\alpha=0$ ,  $\beta=1/2$ ) is employed, and the dependent scaling field  $h_3$  is represented by the truncated Landau expansion (Eq. (8.1.13)). While the LLT graph is likely curved in the pressure–temperature domain (see Fig. 8.5), the author adopted a LLT linearisation, discussed the accuracy and justification of several model approximations, and evaluated the sensitivity of the location of the LLCP against several constraints (reference to the method of Holten et al., 2012; see Fig. 8.7 for the location of LLT and LLCP in the  $p$ – $T$  diagram). By fitting the mean-field critical model to experimental property data of supercooled and stable water, a set of parameters for the equation of state was derived (Tab. 8.2) which allows the complete evaluation of the mean-field approximation model for the determination of isothermal compressibility, the expansivity coefficient, and the isobaric heat capacity according to Eqs. (8.2.8), (8.2.9), (8.2.10). It was found that at atmospheric pressure the isochoric heat capacity becomes negative and diverges at about 229 K, hence the liquid becomes thermally unstable below that temperature (see p. 82).

The author extended the model in such a way that all experimental data of supercooled water up to the pressure of 400 MPa can be represented. However, as far away from the critical point the predictive power (and influence) of the scaling relation Eq. (2.2.1)) decreases and the non-critical regular part of the model dominates the thermodynamic properties, the author empha-

sised that such an extension of the scaling relation Eq. (2.2.1)) should be regarded as semi-empirical.

It was shown that a mean-field approximation of the theory of critical phenomena is able to capture the anomalous thermodynamic properties of supercooled water with the same accuracy (and with the same number of adjustable parameters as the scaling theory). However, this insensitivity of the results to the particular form of the equation of state is not an argument against the more advanced scaling theory. It is just a consequence of the lack of experimental in the region asymptotically close to the critical point (see p. 88). The author concluded that the exact location of the LLCPP requires independent information for the characterisation of the LLT line! Anyway, the scaling theory imperatively predicts that the thermodynamic response function must contain polynomial terms with divergent critical behaviour.

**Chapter 8 contains a comprehensive survey of mean field approximations of the equation of state of supercooled water. This chapter completes the scientific core of the study and will allow us to draw the following conclusions:**

- **From the different theories (and/or their approximative realisations) it is possible to formulate well-defined requirements on dedicated experiments in the supercooled region. There exist well-defined working hypotheses, providing experimentalists with guidance for future experiment setup to better restrict model assumptions.**
- **In order to guide potential users with respect to the appropriate choice of a model and/or its specific parameters, dedicated and comprehensive model intercomparison studies are necessary.**

**As a member of IAPWS I can only recommend to embed these activities in our community too.**

9. In her final **Chapter 9** the author gave a meaningful summary of their study and fortunately, an outlook on future work. **If I could express a desire from a meteorological point of view, I would also place on the agenda the determination of non-thermodynamic properties such as interfacial energies of liquid/ice, liquid/substrate, and ice/substrate interfaces, which are of very high importance for cloud freezing processes. This subject is to a large extent also unknown ground.**

## 2.3 Specific Comments to the Scientific Part

1. I found the description of the Ising model (the “Drosophila” of statistical physics) in Section 2.2 a little bit spare. The author could have felt free to include more details, at least qualitatively. For example, the author introduced the Heisenberg model for the configurational energy, but omitted its explanation/interpretation. As the Ising model has its historical roots in the description of ferromagnetism, the essential hypothesis that “all fluids exhibit Ising-like asymptotic critical behaviour” is (for me) far away from being trivial. How this hypothesis is supported?
2. On p. 19 the author wrote that the universal critical exponents are measured in various experiments, e. g., from light-scattering data in aqueous electrolyte solutions. How “universal” (or fundamental) are the critical values given in Tab. 2.2? Can these parameters be traced back to more fundamental physical constants? The described universal scaling behaviour is far away from being trivial or self-explanatory.
3. The classical values  $\alpha=0$  and  $\beta=1/2$  refer to the “mean-field approximation” (see p.68). Therewith one obtains the classical limit of the scaling relation Eq. (2.2.1). On the other side, the classical behaviour is described by the Landau theory (Section 2.1). At the critical point the Landau order parameter and the scaling fields vanish, i. e.,  $\varphi = 0$  and  $h_1 = h_2 = h_3 = 0$ . Is there any direct relation between Landau’s order parameter and the scaling fields?
4. In Section 4.3 the author presented the Fuenetevilla–Anisimov scaled equation of supercooled water, which is based on data from Mishima et al. [1] (see p. 33). Later, the author presented the model of Mishima [17] (based on mass density measurements of water at about 200–275 K and 40–400 MPa), who “used the model of Fuentevilla and Anisimov” (see p. 35). However, Mishima’s ordering field is linear in pressure, but non-linear in temperature (Eq. (4.3.10)). Do we know how the predicted Widom lines (Eqs. (4.3.3), (4.3.9)) obtained by both models differ from each other?
5. How did the author derive their Eq. (5.1.4) for the molar isobaric heat capacity of the vapour,  $C_{p,\text{vap}}$ , from the paper of Murphy/Koop (2005) (MK05)? I would suggest the following way:

$$\frac{dL_s}{dT} \approx C_{p,\text{vap}} - C_{p,\text{ice}} \rightsquigarrow C_{p,\text{vap}} \approx C_{p,\text{ice}} + \frac{dL_s}{dT} .$$

The molar latent heat of sublimation,  $L_s$ , is given by MK05, Eq. (5). The molar isobaric heat capacity of ice,  $C_{p,ice}$ , by MK05, Eq. (4).

6. The prediction of the molar isobaric heat capacity of the liquid,  $C_{p,liq}$ , from the scaled equation of state suggests (for future studies) the determination of the molar latent heat of melting,  $L_m$ , by integration of Kirchoff's differential equation (employing the expression for the molar isobaric heat capacity of the liquid,  $C_{p,ice}$ ):

$$\frac{dL_m}{dT} \approx C_{p,liq} - C_{p,ice} .$$

The result could be compared with the prediction of Murphy/Koop (2005),  $L_m = L_s - L_e$  (using MK05, Eqs. (5), (9)). It could also be used for comparison with and/or the extension of the  $L_m$  prediction provided by the new TEOS-10 standard provided by IAPWS. Note that the melting enthalpy is an essential thermodynamic property controlling both homogeneous and heterogeneous nucleation of ice. It seems that the differences between different melting enthalpy expressions from the literature are mainly related to uncertainties in  $C_{p,liq}$  rather than in  $C_{p,ice}$ . Here, the present approach could help to bring more clarity.

7. The surface tension of supercooled water is one of the key properties affecting the determination of critical formation energies in ice nucleation. Hence, the sensitivity of the nucleation rate against the surface tension of supercooled water (Eq. (6.2.3) versus (6.2.5)) must be elucidated in further studies. Owing to the invalidity of the singularity assumption employed in Eq. (6.2.3) (standard textbook expression!), such comparison is of high practical importance.
8. The isobaric heat capacity of supercooled water predicted by the Bertrand–Anisimov model (depicted in Fig. 7.1) is worth to be included in the comparison with author's own and previous results (depicted in Fig. 5.4). The same is true for the prediction of the Kalová–Mareš–Anisimov–Sengers (KMAS) model depicted in Figs. 8.1, 8.2. Finally, also the results from the mean-field approximation of the HBAS model (and its modifications described in Section 8.2, see Fig. 8.12) should be included in such intercomparison. I am very anxious to get to know (in future) how the differences in predicted heat capacities affect the melting enthalpy in the “no man's land”.



9. The degree of sophistication of the thermodynamic model (i. e., the degree of nonlinearity and choice of the thermodynamic variables in the dependencies of scaling fields on the physical fields) depends on the “symmetry” of the system. Is it possible to “scale” the symmetry of a system in terms of any empirical parameter or descriptive notion? What is the evaluation criterion for the degree of symmetry?

## 2.4 Technical Comments

1. P. 6, Fig. 1.1: There are two (lower and upper) thermodynamic limits of stability (thermodynamic spinodals),  $T_{S,1}$  and  $T_{S,2}$ , and two (lower and upper) kinetic limits of stability (kinetic spinodals),  $T_{H,1}$  and  $T_{H,2}$ , respectively.
2. At the critical point, all scaling fields are equal to each other (as written on p. 18), but moreover, they are also equal to zero.
3. P. 20, Eq. (2.2.12): The isothermal compressibility,  $\kappa_T$ , is employed but not yet introduced here.
4. P. 34, Fig. 4.1: There is no reference to this figure in the text (and no interpretation). I suspect that  $C_1$  refers to the vapour–liquid critical point, and  $C_2$  to the LLC. Does the line passing through  $C_2$  refer to the Widom line given by Eq. (4.3.3)?
5. P. 34, Eqs. (4.3.4), (4.3.5): The parameter  $(a_1)_{\text{eff}}$  appearing in the Fuentesvilla–Anisimov model (scaled equation of state) is not explicitly defined here. However, later on p. 67, Eq. (8.1.6), a property  $a_{1,\text{eff}}$  with seemingly the same physical meaning has been defined.
6. P. 36, Eqs. (4.3.12), (4.3.13): There are two minor typos.
7. P. 40, Eq. (5.1.2): The term  $\Delta C_p$  must be correctly written as  $\Delta C_p = C_{p,\text{vap}} - C_{p,\text{liq}}$  (see for example Pruppacher/Klett (1997, p. 116, Eqs. (4-76), (4-77)) (PK97). Consequently, the sign in Eq. (5.1.7) must be changed. Therewith, one arrives at the following result:

$$\frac{dL_e}{dT} = \begin{cases} < 0, & -45^\circ\text{C} \leq \vartheta \leq 40^\circ\text{C}, \text{ PK97, Eq. (3-24a), Fig. 3-12,} \\ > 0, & -150^\circ\text{C} \leq \vartheta \leq -106^\circ\text{C}, \text{ Murphy/Koop (2005, Fig. 1)} \end{cases}$$

Later, Eq. (5.2.3) (Clausius–Clapeyron equation) is correctly written.

8. P. 43, at the end: The correct figure reference here must be Fig. 5.5. This figure is in agreement with my comment on  $dL_e/dT$  in the previous item (i. e., there is just a typo in  $\Delta C_p$  but not a calculation error).
9. P. 50, Eq. (6.2.3), Fig. 6.4: The value of the coefficient  $a_1$  in Eq. (6.2.3) is questionable. In Pruppacher/Klett (edition 2010, ISBN 978-0-7923-4211-3, Eq. (5-12)), the coefficient reads  $a_1=0.115$ , all others are the same as in Eq. (6.2.3).
10. P. 72, Fig. 8.3: I guess it is the isothermal compressibility,  $\kappa_T$ , which is depicted here.
11. P. 82, 86, Fig. 8.12: There is no references to Fig. 8.12 in the text; reference must be inserted on p. 82.
12. P. 81: I suggest reference to Fig. 8.6 must be replaced with Fig. 8.7 here.

### 3 Final comment

I found this study very interesting, the employed methods very instructive, the results very nutritive, and the reading very enjoyable. The presented work is an important contribution, among others, to “hot spots” in atmospheric chemistry and physics. The employed theoretical approaches enlarge our arsenal of methods to describe metastable states and phase transitions of water in Earth’s (and extrasolar planet’s) atmosphere. My respect and congrats to the author!

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