

ABSTRACT

Title of thesis: **A SCALED PARAMETRIC EQUATION OF STATE
FOR THE LIQUID-LIQUID CRITICAL POINT
IN SUPERCOOLED WATER**

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The second-critical-point scenario is one of the most popular explanations for the anomalous behavior of supercooled liquid water. According to this scenario, liquid water at ambient conditions is a "supercritical" fluid that separates into two types of liquid water in the supercooled region. However, experimental confirmation is challenging. In this work we developed a scaled parametric equation of state, based on the principle of critical-point universality, to examine the second-critical-point scenario from a new direction. The equation of state, built on the growing evidence for liquid-liquid water separation, is universal in terms of theoretical scaling fields and belongs to the Ising-model universality class. The theoretical scaling fields are postulated to be analytical combinations of the physical fields, pressure and temperature. The equation of state enables us to accurately locate the "Widom line" (locus of stability minima) and determine that the critical pressure is considerably lower than predicted by computer simulations.

A SCALED PARAMETRIC EQUATION OF STATE FOR THE
LIQUID-LIQUID CRITICAL POINT IN SUPERCOOLED WATER

by

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Nomenclature

U	Energy
S	Entropy
V	Volume
N	Number of molecules
X	Canonical independent variable for the energy
$\xi = \left(\partial U / \partial X_j \right)_{X_1, X_2, \dots, X_{j-1}, \dots, X_{n+2}}$	Conjugate intensive variables (temperature, minus pressure, chemical potential)
T	Temperature
C_V	Isochoric heat capacity
κ_T	Isothermal compressibility
C_P	Isobaric heat capacity
LDA	Low density amorphous water
HDA	High density amorphous water
LDL	Low density liquid water
HDL	High density liquid water
T_S	Spinodal (singular) temperature
X_b	Regular background
α_P	Thermal expansivity
TMD	Temperatures of maximum density
ρ	Density
μ	Chemical potential (Gibbs energy per molecule)
A	Helmholtz energy per molecule
χ	Isothermal susceptibility
X_c	Subscript c indicates critical-point value of the property X e.g. T_c , P_c , ρ_c critical temperature, pressure, and density
$\hat{X}$	Circumflex accent above indicates dimensionless property $\hat{T} = \frac{T}{T_c}, \quad \hat{\rho} = \frac{\rho}{\rho_c}, \quad \hat{P} = \frac{P}{\rho_c k_B T_c}, \quad \hat{\mu} = \frac{\mu}{k_B T_c}, \quad \hat{A} = \frac{A}{k_B T_c},$ $\hat{S} = \frac{S}{k_B}, \quad \hat{C}_P = \frac{C_P}{k_B}, \quad \hat{C}_V = \frac{C_V}{k_B}, \quad \hat{\kappa}_T = \rho_c k_B T_c \kappa_T, \quad \hat{\alpha}_P = T_c \alpha_P,$ $\hat{\chi} = \frac{\chi}{\rho_c k_B T_c}$

ϕ	Order parameter
$h_3 = f(h_1, h_2) = \phi_1 dh_1 + \phi_2 dh_2$	Critical part of field-dependent “theoretical” thermodynamic potential
h_1	“Ordering” field
h_2	“Thermal” field
ϕ_1	Ordering parameter – conjugate, strongly fluctuating theoretical scaling density
ϕ_2	Conjugate, weakly fluctuating theoretical scaling density
$f^\pm$	Scaling function where $\pm$ refers to $h_2 > 0$ and $h_2 < 0$, respectively
$\approx$	Asymptotically equal
$\simeq$	Approximately equal
$\equiv$	Identically equal
$\alpha, \beta, \gamma, \nu, \delta, \eta$	Universal critical exponents
$\hat{A}_0, \hat{B}_0, \hat{\Gamma}_0^\pm$	Ising critical amplitudes
χ_1	“Strong” scaling susceptibility
χ_2	“Weak” scaling susceptibility
χ_{12}	“Cross” scaling susceptibility
γ	Critical exponent
d	Spatial dimensionality in renormalization group theory
n	Number of components of the order parameter (order parameter dimensionality)
IAPWS	International Association for the Properties of Water and Steam

CHAPTER 1

INTRODUCTION

The simple chemical formula and ubiquity of water belie the challenges involved in understanding its behavior. Although water plays a critical role in our understanding of such phenomena as weather, sound propagation for communication, and geo- and bio-evolution, current science does not fully explain water's observable behavior.¹ One of the most significant challenges is describing the behavior of supercooled liquid water. Upon supercooling, water exhibits anomalous behavior with sharply increasing heat capacity, isothermal compressibility, and the magnitude of negative thermal expansivity.¹ However, exhaustive experimental exploration of the behavior of supercooled liquid water is hampered by thermodynamic and kinetic limits of stability.² While experimental data for liquid water behavior at stable temperatures and pressures are readily available,³ the limited experimental data on supercooled water highlight the need for a thermodynamically consistent equation of state to describe the behavior of water into the supercooled region. Figure 1 shows the phase diagram for water as well as the limits for empirical equations of state^{3, 4} and experimental measurements in the supercooled region.

Several competing theories, consistent with the limited data available, explain the anomalies in supercooled liquid water.¹ One of the leading theories, the second-critical-point scenario, proposes a liquid-liquid critical point in supercooled water.⁵ This scenario suggests the existence of two liquid waters, characterized by high density and low density, and proposes that their coexistence curve terminates

in a critical point. According to the second-critical-point scenario, liquid water at ambient temperature and pressure is a supercritical fluid, as the difference between two fluid phases disappears beyond the critical point and the fluid becomes homogenous.

The thermodynamic behavior of a fluid in the vicinity of a critical point is described by a field of physics called critical phenomena. The modern theory of critical phenomena describes the behavior near the critical point with a universal equation of state based on theoretical variables. These theoretical variables can be mapped into real physical variables through so-called "complete scaling," an approach that allows for accurate application of the theory of critical phenomena to real fluids.⁶ We are going to apply this theory to the theorized second-critical-point and use this new perspective on the observed behavior of supercooled water to draw new conclusions about the validity of the scenario and the possible location of this second critical point. Although this scenario has been explored with some limited experiments and with simulations of water-like models, a thermodynamically consistent equation of state based on critical phenomena has not yet been developed. Unlike other approaches, an equation of state developed with the application of complete scaling would depend on only three adjustable parameters, the critical pressure, the system dependent amplitude k/a , and the non-critical background, and provide a way of predicting behavior in the supercooled region.

This thesis examines the problem of thermodynamic consistency of the second-critical-point scenario using the physics of critical phenomena. We present a scaled parametric equation of state based on the principle of critical-point universality in

order to describe and predict thermodynamic properties of supercooled water. In the course of developing the equation of state we also answer the following questions:

1. If the critical point in supercooled liquid water exists, where is it located?
2. What is the nature of the criticality at the critical point, mean-field or fluctuation dominated?
3. If the critical point is fluctuation dominated, what is its universality class?

Our equation of state is built on the assumption that the critical point of liquid-liquid separation in supercooled water does exist, and that the critical anomalies are associated with the critical fluctuations of the appropriate order parameter and exist wherever the correlation length exceeds the range of molecular interactions. This equation of state is universal in terms of theoretical variables and belongs to the three-dimensional Ising-model class of universality. The theoretical scaling fields are postulated to be analytical combinations of physical fields (pressure and temperature). The equation of state enables us to accurately locate the "Widom line"⁷ (the locus of stability minima and maxima of order-parameter fluctuations) and the position of the critical point, as well as to predict thermodynamic properties in the regions that may not be accessible to experiments. The liquid-liquid critical point is also predicted for heavy water. In particular, we conclude that the theory of critical phenomena does not invalidate the possibility of a second critical point in supercooled liquid water and that the critical pressure for the second critical point must be considerably lower than the critical pressure obtained from computer simulations. In the future, other alternative scenarios, such as the singularity-free

scenario and the possibility of multiple liquid-liquid critical points in supercooled water will also be analyzed and compared with experimental data. Moreover, possible effects of the existence of the second critical point in supercooled water on the anomalous behavior observed in some aqueous solutions at ambient conditions as well as liquid-phase polymorphism in other substances, will be considered in future research.

This thesis is organized into six chapters, beginning with the introduction. Chapter II covers supercooled liquid water as it is currently understood, including the challenges in experimentally exploring the supercooled region, existing experimental data and its accuracy, and the leading theories for the anomalous behavior. Chapter III introduces the thermodynamics of critical phenomena through discussion on the nature of the critical point, the universality of critical phenomena and the scaled equation of state, classes of universality, and the translation of the theoretical equation of state to physical variables. Chapter IV describes the development of the parametric scaled equation of state for supercooled liquid water, based on the choice of the three-dimensional Ising-model class of universality, the particular form of the analytic relationship between physical and scaling fields, and the simplification of the equation of state through a particular choice of critical entropy. Chapter V presents our results, describes the limitations of the mean-field approximation, and shows comparisons between the thermodynamic properties predicted by the scaled equation of state and existing experimental data. Implications of the scaled parametric equation of state for the second-critical-point scenario are discussed. Chapter VI summarizes the conclusions and suggests future work.

The principle results of this study have been announced in a Physical Review Letter.⁸

CHAPTER 2

SUPERCOOLED LIQUID WATER: WHAT IS KNOWN AND WHAT IS THEORIZED

2.1 Supercooled Liquids in General

Supercooled liquids are metastable with respect to a solid phase and remain liquid only because they lack the activation energy to transition to the lower global free energy of the solid phase. Kinetic effects such as vibrations, suspended impurities, or even contact with the surface of a container can provide the activation energy required for the new phase to appear before the thermodynamic stability limit is approached. These experiment-dependent properties affect the limit of kinetic stability. The deeper the supercooling, the larger the energy difference between the two states, and the more likely the energy barrier prohibiting phase change will be overcome either through spontaneous thermal fluctuations or with the help of an activator. The point at which inherent thermal fluctuations of the material overcome the energy barrier to a phase change represents the kinetic limit of stability for a supercooled liquid.

In any experimental observation of supercooled liquid water, both kinetic and thermodynamic effects influence the degree of supercooling which can be achieved. A schematic of the thermodynamic and kinetic limits on supercooling is shown in Fig. 2.

Kinetic Limits on Supercooling. The characteristic rates and mechanisms define the kinetic limits of stability for particular systems. In order to study the supercooled

fluid, its lifetime must be longer than the observation time. There must be an experimentally accessible time scale intermediate to the systems lifetime and any measured properties internal relaxation time in order to characterize the fluid. In other words, the system must be in equilibrium for the duration of the observation time. When these conditions are met, the system can be examined thermodynamically.²

Suspended impurities, vibrations and imperfect boundaries provide higher energy surfaces for the formation of a new phase. A phase change in the presence of these imperfections is known as heterogeneous nucleation. If no imperfections are present, the new phase can still form within the bulk of the metastable fluid in a process known as homogeneous nucleation. In homogeneous nucleation, a new phase is formed when thermal fluctuations overcome the free energy barrier and form a crystal of a critical size.²

With a short enough time scale for cooling, even the homogeneous nucleation limit for supercooling can be avoided. Liquids that have been cooled on a time scale shorter than the time required for phase change are kinetically arrested in a metastable amorphous structure and become "glassy." The temperature upon cooling at which they become glassy is referred to as the glass transition temperature. Upon warming, the temperature when the glass has enough energy to complete the phase change to a stable crystal structure does not typically occur at the same temperature as the glass transition and is referred to as the spontaneous crystallization temperature.

Thermodynamic Limits. The thermodynamics of supercooled liquid water include both phenomenological or traditional thermodynamics and mesoscopic thermodynamics. Traditional thermodynamics determines bulk properties from a macroscopic perspective. Stability criteria, given by thermodynamic inequalities and equilibrium conditions, imply a sharp, absolute boundary between phases. Mesoscopic thermodynamics recognizes that thermal fluctuations within the bulk substance imply that stability criteria be treated statistically.⁹

For the equilibrium state to be stable, the energy of the equilibrium state, U , must be at a minimum for all variations subject to constant entropy (S), volume (V), and number of molecules (N). Phenomenologically, the general stability criteria of a pure fluid are:

$$\partial^2 U \left(\frac{\partial \xi_2}{\partial X_2} \right)_{\xi_1, X_3} \geq 0 \quad (2.1)$$

where X represents the canonical independent variable for the energy (S, V, N) and ξ represents the conjugate intensive variables (temperature, minus pressure, chemical potential). The conjugate intensive variables are obtained by partial differentiation:

$$\xi_j = (\partial U / \partial X_j)_{X_1, X_2, \dots, X_{j-1}, X_{j+1}, \dots, X_{n+2}}.$$

Expressing the criteria in measurable quantities, we find that positive values of the isochoric heat capacity, C_V , or the isothermal compressibility, κ_T , are necessary and sufficient for stability:

$$\left(\frac{\partial T}{\partial S} \right)_{V, N} = \frac{T}{C_V} \geq 0, \quad (2.2)$$

$$\left(-\frac{\partial P}{\partial V} \right)_{T, N} = \frac{1}{V \kappa_T} \geq 0. \quad (2.3)$$

In other words, the temperature of stable fluids, T , must increase with the addition of heat or the pressure must increase if the body is compressed. The thermodynamic limit of stability is not accessible experimentally, since the kinetic limit will always be reached first.

The stability equations describe the stability of a fluid with respect to another amorphous phase. They arise from considering fluctuations that appear to exhibit different intensive properties than the bulk fluid but are locally in equilibrium. However, supercooled liquids are metastable with respect to an ordered, translationally modulated or solid phase. The limits of stability of a fluid phase with respect to a solid phase have not yet been developed.²

Although the location of the thermodynamic limit on supercooling is more uniformly applicable to various experimental setups than the kinetic limits, which depend on experimental conditions, the thermodynamic limit still requires an accurate equation of state. Until a thermodynamically consistent equation of state for liquid water exists, the location of the thermodynamic limit on supercooling remains uncertain.

2.2 Supercooled Liquid Water

Most liquids show no significant change in properties when driven into a metastable state and show no evidence of approaching a condition of impending loss of stability. In particular, the heat capacity and isothermal compressibility of most liquids do not increase anomalously below freezing temperatures. In fact, the

response functions of most liquids decrease upon supercooling until freezing or vitrification occurs. The anomalous behavior of supercooled liquid water, therefore, can not be fully explained in terms of typical liquid behavior and our current depiction of the phase diagram (Fig. 1).

In 1971, Alexander Voronel speculated that the liquid phase could be defined as a state between two singular points.¹⁰ Investigating this hypothesis, Anisimov *et al.* used an adiabatic calorimeter to measure the isobaric heat capacity, C_P , of water in the supercooled region (Fig. 3). Although the degree of supercooling was modest (reaching $\sim -8^\circ\text{C}$), measurements showed a noticeable increase in the isobaric heat capacity of metastable water upon supercooling.¹¹ In that work, the authors interpreted the observed anomaly as associated with a singularity in the supercooled state and even estimated the temperature at which C_P would diverge (255 K). It was not known at that time that the observed anomaly is associated with the unique phase behavior of water in the supercooled state, a major scientific challenge in the subsequent three decades.¹ Two years later, Angell, Shuppert, and Tucker performed accurate heat-capacity measurements of 1 μm droplets of supercooled water emulsified in *n*-heptane¹² using a procedure first developed by Rasmussen and MacKenzie.¹³ Reaching temperatures as low as -39°C , Angell and co-workers observed a sharp increase in the isobaric heat capacity that resembled a critical-point-like singularity (Fig. 4).

In addition to anomalies in heat capacity, subsequent experiments found that the isothermal compressibility and the thermal-expansion coefficient also exhibit critical-like anomalies with the isothermal compressibility¹⁴ increasing and the ther-

mal expansivity¹⁵ sharply decreasing upon supercooling. Anomalies also appear in most transport properties and dynamic properties.¹

Since the anomalies in the thermodynamic properties of supercooled liquid water increase with supercooling, accurate, reliable experimental data for deeply supercooled water are important. There are two possible approaches to experimentally examining deeply supercooled liquid water and avoiding heterogeneous nucleation: carefully cool very pure samples of water below the freezing point or slowly heat glassy water above the glass transition temperature.

The experimental data collected to date suggest that the kinetic limits on supercooling liquid water exist around -42°C ($\sim 231\text{ K}$).^{16, 17, 18} In order to obtain data at these low temperatures and avoid crystallization, much of the experimental evidence for the anomalous behavior of supercooled liquid water was obtained from small volumes of water in capillary tubes or micro emulsions. Although small samples are easier to supercool than bulk water, the effects of surface energy would have a magnifying effect on perceived anomalies. Several studies have looked at the relevance of this data to bulk water behavior.^{19, 15, 20} Although the effect of surface energy cannot be completely discounted, these studies have shown that the same anomalous behavior exhibited in the small samples also exists in bulk water. Roughly calculated, 0.6% of the molecules in a $1\text{ }\mu\text{m}$ droplet are present in the outer $10\text{ }\text{\AA}$ of the droplet. Tombari *et al.*²⁰ and Angell and co-workers, using adiabatic calorimetry, confirmed the emulsion data for bulk water (10 cm^3) that remained uncrystallized to -30°C .

There are also kinetic limits imposed when approaching the metastable liquid

region by slowly heating glassy water. Below the homogeneous nucleation limit of around -42°C (231 K) and above the kinetic limit of spontaneous crystallization of glass, around -123°C (150 K),^{21, 22} there is a region of "no man's land," in which the time scale of the system stability precludes experimental measurements (Fig. 5).

Although the region directly above the spontaneous crystallization to ice Ic, is unavailable to experiments, the form of glassy water, or amorphous ice, directly below this limit offers insight to the possible behavior of supercooled liquid water in no man's land. Glassy water is formed by cooling liquid water below the stable range faster than it crystallizes, kinetically arresting its structure. Water, unlike most substances, forms at least two distinct forms of glass: low density amorphous water (LDA)²³ and high density amorphous water (HDA).^{24, 25, 26} Although LDA and HDA amorphous ice are very solid (Fig. 6), their structure is disordered and they transform into highly viscous liquids above the glass transition temperature of 136 K.^{21, 27, 28, 29} Experimental measurements of the transition between LDA and HDA support an apparent first-order transition (Fig. 7).³⁰ However the experimental difficulties in working close to the kinetic limits leave some room for debate as to whether the observed differences are due experimental methods or distinct phases of amorphous water.³¹ Any theory explaining the anomalous behavior of supercooled liquid water must also explain glassy water.

2.3 Three Scenarios for Supercooled Liquid Water

The existence of these two types of amorphous ice and the anomalous behavior of liquid water do not yet fit into any widely accepted thermodynamically

consistent theory. The difficulty in exploring the phase behavior of liquid water at low temperatures has limited the availability of experimental data and left an incomplete picture of physical cause behind these anomalies. There are currently three competing interpretations: the stability limit conjecture, the singularity-free scenario, and the critical point scenario.

The Stability Limit Conjecture. The stability limit conjecture, introduced by Speedy in 1982,³² proposes that the liquid-vapor spinodal turns toward positive pressures in the supercooled region of liquid water, connecting superheated and supercooled states, at the intersection with the locus of density maxima (Fig. 8). The presence of the spinodal, a locus of diverging density and entropy fluctuations,² predicts power-law behavior of properties,

$$X = A \left(\frac{T}{T_s} - 1 \right)^{-x} + X_b, \quad (2.4)$$

where X is a property that diverges at the spinodal, A is a constant, T_s is the spinodal (singular) temperature, x is an empirical exponent, and X_b is the regular background. This behavior empirically accounts for the observed increase in water’s compressibility,^{33, 14} isobaric heat capacity,³⁴ and other properties.^{33, 35, 36} The water-like lattice model of Sastry *et al.*³⁷ and the lattice-gas implementation of a random graph model of water’s hydrogen-bonded network of Sasai,³⁸ provide microscopic validation with possible physical mechanisms accounting for a retracing of the spinodal toward positive pressures. Although the presence of the spinodal

curve, representing instability with respect to the fluid phase, offers a thermodynamically consistent explanation for the increase in response functions, the theory did not originally account for metastability with respect to an anisotropic crystalline phase. The microscopic models or computer simulations account for the instability of supercooled water with respect to the solid phase, predicting that the response functions increase sharply but do not diverge upon supercooling.²

Although the properties of supercooled water can be empirically fit to the power law predicted by the stability limit conjecture, there is a major conceptual problem with this scenario. In order for the liquid-vapor spinodal to maintain a negative slope in the (P, T) plane in the measurable regions of the liquid-vapor coexistence region before curving up toward positive pressures, the spinodal must cross the extension of the liquid-vapor equilibrium curve into the metastable region. Therefore, in order for the liquid-vapor spinodal to curve back to positive pressures, the metastable extension of the liquid-vapor equilibrium curve must terminate in a lower liquid-vapor critical point (Fig. 9). Although there are microscopic models showing a spinodal curve toward positive pressures when crossing the line of temperatures of maximum density (TMD) for any given pressure,^{37, 38, 39} there is not currently any evidence supporting the predicted lower liquid-vapor critical point.

The Singularity-Free Scenario. The behavior of the density is probably the most widely known anomaly of liquid water. At atmospheric pressure, the density of liquid water reaches a maximum around 4°C and then decreases upon cooling (Fig. 10). This behavior can be attributed to the cohesive nature of the hydrogen bond

network and the entropy associated with the expanded and collapsed network structures.^{40, 41} According to the singularity-free scenario, the experimentally observed increases in the response functions of liquid water upon supercooling can be accounted for through the density anomalies and, ultimately, the hydrogen bond network which provides water its unique density properties.^{42, 43, 44} Isobaric heat capacity, C_P , isothermal compressibility, κ_T , and thermal expansivity, α_P , all depend on density, ρ , through the relevant thermodynamic relations,

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{T}{\rho^2} \left(\frac{\partial^2 \rho}{\partial T^2}\right)_P, \quad (2.5)$$

$$\kappa_T = \frac{1}{\rho} \left(\frac{\partial \rho}{\partial P}\right)_T, \quad (2.6)$$

$$\alpha_P = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T}\right)_P, \quad (2.7)$$

while the TMD is negatively sloped in the (P, T) plane. Therefore, with the density anomaly, the isothermal compressibility of liquid water increases upon isobaric cooling, the thermal expansion coefficient increases upon isothermal compression and becomes negative upon isothermal decompression, and the isobaric heat capacity decreases upon isothermal compression.¹ The anomalous negatively sloped TMD locus therefore predicts increases in the response functions, which may remain finite,⁴⁵ without suggesting any singularities.⁴⁴

The singularity-free scenario is supported by several models which show anomalous increases in response function without a corresponding singularity. Stanley *et al.*^{46, 47, 48} proposed a microscopic model based on bond formation between neighboring molecules, which predicted density fluctuations and finite anomalies in

thermodynamic properties. Sastry *et al.*^{42, 44, 49} introduced a lattice model with nearest-neighbor attraction and directional attractions that also predicted finite increases in the response functions. The lattice model of Borick *et al.*³⁹ shows a retracing density maxima locus but no evidence of singularities or a retracing spinodal. In addition to these models, small angle X-ray scattering experiments conducted by Xie *et al.* show no anomalous growth the correlation length to suggest the presence of a singularity.⁴⁵

However, other models are more ambiguous. A field-theory model of water's hydrogen bond network by Sasai does not predict any singularities above the liquid-ice spinodal, but it does shown the response functions diverging along the liquid-ice spinodal.⁵⁰ The model of Truskett *et al.* generates either a singularity-free scenario or a liquid-liquid critical point in supercooled water depending on the choice of parameters.⁵¹ Even X-ray scattering experiments are not conclusive due to the weak scattering in supercooled water. The long accumulation times, separation of critical behavior and non-critical background, and specific cell geometry cause significant experimental errors,⁴⁵ while some studies show an increase in the correlation length⁵² that does not support the singularity-free scenario.

The Second Critical Point Scenario. In 1992, Poole *et al.* proposed that the observed anomalies in supercooled liquid water are associated with density and entropy fluctuations diverging at a critical point of liquid-liquid coexistence.⁵ This critical point terminates a line of first order phase transitions between two liquid phases: low-density liquid (LDL) and high-density liquid (HDL). The experimentally ob-

served LDA and HDA are interpreted as structurally arrested glassy forms of these two liquid phases.^{53, 54, 55} Linking the anomalies of supercooled liquid water to the phase transition between LDA and HDA, the "second-critical-point" scenario presents as thermodynamically consistent view on the global phase behavior of supercooled water.

According to this view, the liquid-liquid coexistence curve in supercooled water has a negative slope in the (P, T) plane, differing from the more common positive slope seen with the liquid-vapor coexistence curve (Fig. 11). As a result, water at ambient temperatures and pressures is a supercritical fluid and "above" the liquid-liquid critical point where the metastable fluids LDL and HDL become indistinguishable. Below the critical point, at lower temperatures and higher pressures, LDA and HDA separate (Fig. 12). As both fluids are metastable with respect to the solid crystal, transient domains of long-range tetrahedral symmetry form spontaneously due to thermal fluctuations.^{46, 56} The lower surface interaction energy between like structures favors larger domains of these lower density, ordered tetrahedral structures. The transition from the lower density, ordered LDL to the higher density disordered HDL corresponds to a change from an energy driven to an entropy driven structure of the hydrogen bond network. The negative slope in the (P, T) plane of the phase transition locus is due to the higher entropy of the high density phase. The liquid-liquid transition is also different from the liquid-vapor curve with a large slope in the (P, T) plane at the critical point (about 30 times larger than the liquid-vapor transition), which indicates the significance of the entropy change with respect to the density change, and, correspondingly, a greater

importance of the entropy fluctuations.

The hypothesis of a second-critical-point scenario is supported by extensive Monte Carlo and molecular dynamic simulations of various water and water-like models,^{37, 57, 58, 59} and by a modified van der Waals model that includes hydrogen-bond contributions.^{60, 51} Limited but impressive experimental evidence for the existence of the liquid-liquid critical point in supercooled water was obtained by Mishima and Stanley.^{61, 62} They observed that the melting curve of metastable ice IV undergoes a sharp change of slope in the region where it would intersect the expected liquid-liquid transition. Moreover, similar measurements performed for several forms of D₂O ice showed a decrease in the slope change with decreasing pressure upon approaching the hypothesized critical point.⁶³ Based on their experiments, Mishima and Stanley⁶¹ constructed a Gibbs-energy surface for supercooled water and estimated the location of the critical point at approximately 1 kbar and 220 K. The equation of state obtained by differentiation of the constructed Gibbs-energy surface is very inaccurate. Therefore, it is not surprising that the exact location of the liquid-liquid critical point, especially the value of the critical pressure, is uncertain. The simulation data of various water-like models yields a variety of the critical-pressure values, from negative pressures to 3.4 kbar¹ (Fig. 13). On the other hand, according to Fig. 7 by Mishima, the critical pressure in D₂O is most likely located below or around 0.5 kbar.⁶³

In general, the second-critical point scenario appears more plausible than either the stability limit conjecture or the singularity-free scenario, especially in

view of the experimental evidence of a first-order phase transition between two amorphous-water glasses, LDA and HDA. However, conclusive evidence of the second-critical-point scenario requires further experimental studies such as quenching on droplets small enough to avoid crystallization and accurate measurements of the heat capacity in supercooled water at high pressures.¹

CHAPTER 3

CRITICAL PHENOMENA

3.1 Phase Transitions and the Critical Point

Critical phenomena is the field of physics describing the behavior of substances near second-order phase transitions, also known as critical points. Critical points terminate a line of first-order phase transitions, also known as a coexistence curve. First-order phase transitions can be defined by the continuous change in thermodynamic potential and the discontinuity in the first derivative of the thermodynamic potentials such as entropy and volume through the phase change. Rephrased, intensive properties remain continuous but extensive properties become discontinuous. In first-order phase transitions, the possibility of metastable states exists as the stability limit is located beyond the equilibrium coexistence curve. Second-order phase transitions, however, exhibit discontinuity in intensive properties. The thermodynamic potentials and their first derivatives, such as molar volume, molar entropy, molar enthalpy, or concentration, are continuous but the second derivative of the thermodynamic potentials, such as molar heat capacity, isothermal compressibility, and thermal expansivity, are discontinuous.⁶⁴ The point where the binodal, or phase coexistence curve, and the spinodal, the limit of stability, coincide is a critical point since there is no metastable state beyond the phase transition in which the thermodynamic quantities can exist (Fig. 14).

Critical phenomena apply to many different types of transitions including phase transitions between some crystal structures, the transitions characterized by

the emergence of magnetism or superfluidity, and the phase transitions in all kinds of fluids. For pure fluids, the critical point terminates the coexistence curve between two fluid phases, usually vapor and liquid. Beyond the critical point the differences between fluid phases disappear and the fluid becomes homogeneous. For one-component fluids, the critical point is specified by the critical temperature T_c , critical density ρ_c , and critical pressure P_c . For convenience, the dimensionless thermodynamic properties are defined differently than the typical definitions for a liquid-vapor critical point (see Section 3.3). The thermodynamic properties reduced by the critical parameters are defined as follows:

$$\begin{aligned}
\hat{T} &= \frac{T}{T_c}, & \hat{\rho} &= \frac{\rho}{\rho_c}, & \hat{P} &= \frac{P}{\rho_c k_B T_c}, \\
\hat{\mu} &= \frac{\mu}{k_B T_c}, & \hat{A} &= \frac{A}{k_B T_c}, & \hat{S} &= \frac{S}{k_B}, & \hat{C}_P &= \frac{C_P}{k_B} \\
\hat{C}_V &= \frac{C_V}{k_B}, & \hat{\kappa}_T &= \rho_c k_B T_c \kappa_T, \\
\hat{\alpha}_P &= T_c \alpha_P, & \hat{\chi} &= \left(\frac{\partial^2 \hat{P}}{\partial \hat{\mu}^2} \right)_{\hat{T}} = \left(\frac{\partial \hat{\rho}}{\partial \hat{\mu}} \right)_{\hat{T}} = \hat{\rho}^2 \hat{\kappa}_T,
\end{aligned} \tag{3.1}$$

where μ is the chemical potential (Gibbs energy per molecule), P is the pressure, S is the entropy per molecule, C_V is the isochoric heat capacity per molecule, A is the Helmholtz energy per molecule, and $\hat{\chi}$ is the isothermal susceptibility. In the (P, T) plane the critical point manifests as the point terminating the coexistence curve. In the (T, V) plane the critical point manifests as the point where the specific volumes of the equilibrium phases coincide (Fig. 10). According to

the critical-point-scenario for supercooled water, above P_c and below T_c water separates into two metastable fluids, LDL and HDL. Water at ambient pressure and temperature exists beyond the critical point and is a supercritical fluid where LDL and HDL become indistinguishable.

The Role of the Order Parameter. Critical points can exist only when the difference between two phases is a matter of degree and a continuous change from one phase to another may occur. In fact, the particular phase of a fluid, liquid or gas, in which coexistence terminates in a critical point, cannot be assigned except in comparison, when both fluids exist simultaneously. A liquid and a gas differ by the degree of interaction between the molecules. A liquid and a solid, on the other hand, differ in their structure, or what Landau and Lifshitz refer to as their “internal symmetry.”⁶⁴ When two substances have different internal symmetry, a defining element, such as a unit cell in a crystal, will exist in one phase but not in the other. This element will not appear gradually during the phase change as it can with substances with the same internal symmetry. There can be no critical point between the two phases of different internal symmetry and the coexistence curve either continues to infinity or intersects with the coexistence curve of another phase.

In addition to the density change between a liquid and gas, critical points can occur between phases where the symmetry element is the displacement of atoms in a crystal resulting in a rearrangement of the crystal lattice or the ordering of the crystal structure changing the probability of finding one type of atom in a particular lattice site. In addition to these symmetry elements, critical points can occur with

a change of symmetry in the elementary magnetic moments of a substance (Curie points of ferromagnetic or antiferromagnetic substances). Another example is the transition of a metal to a state of superconductivity or of liquid helium to a state of superfluidity. In each example, the body changes continuously but acquires a new property at the transition point.⁶⁴

In the 1930's, in order to describe the change in the structure of the body when it goes through a phase transition, Landau introduced the concept of the order parameter, ϕ , which breaks the symmetry of a system at the transition point.⁶⁵ The order parameter is defined as a certain property that is larger in the less symmetrical or disordered phase and smaller or even zero in the disordered phase. If the order parameter is specified as zero in the disordered phase, it becomes finite in the ordered phase. If the order parameter changes at the transition point without discontinuity, the transition is of second order. If the order parameter is discontinuous and exhibits a "jump," the transition is of first order. This definition for the order parameter corresponds to a first derivative of an appropriate thermodynamic potential with respect to the corresponding ordering field, according to the Ehrenfest classification of phase transitions.⁶⁴

For liquid water, an appropriate choice of order parameter is necessary to describe critical phenomena in terms of the general theory of phase transitions.^{66, 67, 68, 69} In principle, any property, like the surface tension, difference in specific or molar volumes, the latent heat - all vanishing at the critical point - can be candidates for the order parameter. However, the correct choice would result in a universal, simplified picture for critical phenomena in physically different systems.

3.2 Universal Critical Phenomena and Scaling Theory

One of the most important results of the study of critical phenomena was the concept of critical-point universality: the discovery that the thermodynamic behavior in the vicinity of a critical point does not depend on the microscopic structure.^{70, 71, 66, 72} Instead, long-range fluctuations of the order parameter, the effect of random deviations from average, dominate over the specific effects of near-neighbor interactions in the critical region. The correlation length, the length scale for the critical fluctuations, diverges at the critical point. Due to this divergence, the thermodynamic properties, functions of the correlation length, become singular at the critical point. Mathematically, the asymptotic critical behavior near critical points is characterized by scaling laws with universal critical exponents and system-dependent amplitudes that are universally interrelated.

The universality of critical phenomena means that critical, or fluctuation induced, behavior can be universally described using theoretical variables, such as the order parameter or the conjugate ordering field, that can be mapped to specific physical variables for different systems. For real fluids and fluid mixtures, it is commonly accepted that the non-analytic critical behavior can be asymptotically described by scaling theory in terms of two independent, theoretical scaling fields, namely, h_1 ("ordering" field) and h_2 ("thermal" field) and two conjugate, theoretical scaling densities, namely, the order parameter ϕ_1 (strongly fluctuating) and ϕ_2 (weakly fluctuating). A third field, $h_3 = f(h_1, h_2)$, is the critical part of the field-dependent theoretical thermodynamic potential, which exhibits a minimum with

respect to a variation of the of the order parameter such that

$$dh_3 = \phi_1 dh_1 + \phi_2 dh_2. \quad (3.2)$$

Scaling theory is based on the assumption that the critical part of the thermodynamic potential h_3 has the form of a non-analytical homogeneous function of the theoretical scaling fields, h_1 and h_2 . Asymptotically:

$$h_3 \approx |h_2|^{2-\alpha} f^{\pm} \left(\frac{h_1}{|h_2|^{2-\alpha-\beta}} \right), \quad (3.3)$$

where $f^{\pm}$ is a scaling function and the superscript $\pm$ refers to $h_2 > 0$ and $h_2 < 0$, respectively. The form of the scaling function is universal for any system; however, it contains two thermodynamically independent (but system-dependent) amplitudes and critical exponents specific to a particular class of systems. All other asymptotic amplitudes are related to the selected ones by universal relations. A salient feature of scaling theory is that the asymptotic behavior of the system near the critical point can be described through a small number of variables, the critical exponents α and β , universal within a class of critical-point universality. All fluids and fluid mixtures belong to the Ising-model class of universality (in which the order parameter is either a scalar or a one-component vector).⁶⁶ The Ising values for α and β , namely $\alpha \simeq 0.109$ and $\beta \simeq 0.326$, are well established theoretically and confirmed experimentally.^{66, 67, 68, 69, 73, 74} The two Ising amplitudes, $\hat{A}_0$ and $\hat{B}_0$ can be de-

terminated by the asymptotic power-law behavior of the two scaling densities in zero ordering field ($h_1 = 0$),

$$\phi_1 = \left(\frac{\partial h_3}{\partial h_1} \right)_{h_2} \approx \pm \hat{B}_0 |h_2|^\beta, \quad (3.4)$$

$$\phi_2 = \left(\frac{\partial h_3}{\partial h_2} \right)_{h_1} \approx \frac{\hat{A}_0^\pm}{1 - \alpha} h_2 |h_2|^{-\alpha}, \quad (3.5)$$

and of the three scaling susceptibilities, "strong" χ_1 , "weak" χ_2 , and "cross" χ_{12} in zero ordering field ,

$$\chi_1 = \left(\frac{\partial \phi_1}{\partial h_1} \right)_{h_2} \approx \hat{\Gamma}_0^\pm |h_2|^{-\gamma}, \quad (3.6)$$

$$\chi_2 = \left(\frac{\partial \phi_2}{\partial h_2} \right)_{h_1} \approx \hat{A}_0^\pm |h_2|^{-\alpha}, \quad (3.7)$$

$$\chi_{12} = \left(\frac{\partial \phi_1}{\partial h_2} \right)_{h_1} \approx \beta \hat{B}_0 \frac{|h_2|^\beta}{h_2} \quad (h_2 < 0), \quad (3.8)$$

where the critical exponent $\gamma = 2 - \alpha - 2\beta \simeq 1.239^{73, 74}$ and the other Ising critical amplitude $\hat{\Gamma}_0^\pm$ is related to $\hat{B}_0$ and $\hat{A}_0^\pm$ through universal ratios, $\alpha \hat{\Gamma}_0^+ \hat{A}_0^+ / \hat{B}_0^2 \simeq 0.0581$, $\hat{\Gamma}_0^+ / \hat{\Gamma}_0^- \simeq 4.8$, and $\hat{A}_0^+ / \hat{A}_0^- \simeq 0.523$.⁷⁴ While the superscript $\pm$ refers to the states at $h_2 > 0$ and $h_2 < 0$, the prefactor $\pm$ in Eq. (3.4) refers to the branches of the order parameter at $h_1 > 0$ and $h_1 < 0$ sides, respectively.

3.3 Classical *versus* Nonclassical (Scaling) Theory of Phase Transitions

Mean-Field Theory. Traditional thermodynamics, which considers only the bulk properties of a homogeneous fluid, is commonly based on mean-field theory. Mean-

field theory neglects thermal fluctuations, simplifying the system until each molecule in the fluid has the fluid's average properties. The complex picture of interactions between particles is replaced by a mean field (or a mean force) that acts equally on all particles. This approximation assumes that the Helmholtz energy is everywhere an analytic function of volume and temperature. The van der Waals theory and other approximate statistical mechanical models are mean-field theories. Mean-field is also known as the simplest solution or zero-order approximation of any statistical mechanical model when a local order is either neglected or considered as a small correction (Ornstein-Zernike approximation). Mean-field theory is a particular case of the more universally applicable scaling theory.

A phenomenological representation of all mean-field theories and models is the Landau theory of phase transitions. The major assumption of the Landau theory is that the thermodynamic potential is an analytical function of an ordering field, h_1 , and a thermal field, h_2 , at the transition point. If so, the critical part of the appropriate thermodynamic potential, h_3 , can be expanded in a power series of the order parameter:

$$h_3 = \frac{1}{2}a_0h_2\phi_1^2 + \frac{1}{4!}u_0\phi_1^4 - h_1\phi_1. \quad (3.9)$$

Above the critical point there is only one solution, $\phi = 0$. Below the critical temperature, there are two solutions with either a positive or negative order parameter.

Mean-Field and Scaling Universal Critical Exponents. Experimentally, it has been well established that asymptotically close the critical point, all physical properties obey simple power laws known as "scaling laws." The universal powers in these

laws are called critical exponents. Both mean-field and scaling theories all result in the divergence of some thermodynamic quantities at the critical point,

$$X \approx A |h_2|^{-k}, \quad (3.10)$$

where k is the critical exponent for a given thermodynamic property X . The exponents that describe this divergence for all mean-field theories are called classical critical exponents. The exponents that describe this divergence and obey the scaling laws are called non-classical critical exponents.

As the simplest solution, mean-field is often used as the first approximation of near-critical behavior. However, the behavior of most fluids near a critical point is dominated by thermal fluctuations and non-classical or macroscopic behavior. As a result, the mean-field approximation breaks down near the fluctuation dependent critical point. Experimentally, real fluid behavior is much more closely described by scaling theory with the nonclassical critical exponents. However, the mean-field approximation becomes exact in systems with long-range interactions such as superconductors. Therefore, when new kinds of critical points are discovered, it is not clear *a priori* whether the critical point is mean-field or fluctuation-dominated.

Renormalization group theory⁷⁵ provides a theoretical method to calculate the critical exponents. According to the renormalization group theory, which is the modern theory of critical phenomena,⁷² the critical exponents of a system depend only on two parameters: the same spatial dimensionality d and the number of components of the order parameter (order-parameter dimensionality) n . Systems

that have the same order-parameter dimensionality belong to the same universality class and can be described by the same set of critical exponents. The order parameter, ϕ_1 , a theoretical variable corresponding to a system-dependent physical quantity, vanishes at the critical point, is nonzero on one side of the transition, and whose fluctuations diverge at the critical point. For pure fluids, the order parameter is mostly associated with the density minus the critical density, $\rho - \rho_c$. The order parameter for pure fluids is zero along the critical isochore, above the critical temperature, and nonzero below the critical temperature, where saturated densities differ from the critical density. Since this order parameter for all fluids is a scalar, its dimensionality n is 1. Fluids, anisotropic magnetic or electric materials, fluid mixtures, binary alloys, and some other systems all belong to the three dimensional Ising-model class universality where $n = 1$, and $d = 3$, and can all be described by the same scaled equation of state asymptotically close to the critical point.

As mentioned earlier, real fluid behavior is inconsistent with the popular mean-field approximation. Therefore, a scaled equation of state, based on the principle of critical-point universality, should be considered for the second critical point in water.

Scaling theory associates all critical anomalies with the divergence of the correlation length. The correlation length plays the role of a "screening length" for the correlation function: when ξ is small, the correlation function is exponentially short-ranged. However, at the critical point, the correlation length diverges and the correlation function becomes long ranged - it decays proportionally with the distance. The amplitude of the order-parameter fluctuations in the correlation

volume is the same as the thermodynamic value of the order parameter in the ordered phase at the same distance to the critical point.

The nonclassical critical values given in Table 1 are the best theoretical estimates of the critical exponents of fluids.^{76, 77} These nonclassical values represent treatment of the system through the correlation function, $G(r)$, a function describing spatial behavior of fluctuations of the order parameter. The correlation function measures how the order parameter at one point correlates to its value at another point at a distance r . If the correlation function decreases quickly with increasing distance between points, then far away points are uncorrelated and the system is dominated by microscopic, short range forces.

The Landau theory satisfies the scaling formulation as far as thermodynamic quantities are concerned and provides us with the nonclassical critical exponents, shown in Table 1. Understanding that all critical anomalies depend on the divergence of the correlation length, the introduced six scaling critical exponents are not independent. The universal relations between the critical exponents for thermodynamic quantities and the correlation length are:

$$3\nu = \gamma + 2\beta \quad (3.11)$$

$$\alpha = 2 - d\nu \quad (3.12)$$

$$\alpha + 2\beta + \gamma = 2 \quad (3.13)$$

$$\gamma = \nu(2 - \eta) \quad (3.14)$$

where d is a space of dimensionality. The equation $\alpha = 2 - d\nu$ does not satisfy the

classical Landau (mean-field) theory for dimensions less than four. In scaling theory only two components and two amplitudes are independent; all other exponents and amplitudes can be calculated through the given two universal relations.

3.4 Translating Theoretical Variables into Physical Variables with "Complete Scaling"

Ising/Lattice Gas Model. The Ising model represents a system of an incompressible lattice where its configuration space (set of possible positions) is the assignment of a +1 or -1 to the otherwise identical vertices on the graph (Fig. 15). In greater than 1 dimension, the Ising model undergoes a phase transition between an ordered and a disordered phase. First proposed by Ernest Ising to represent ferromagnetism,⁷⁸ the Ising model assigned dipoles or "spins" directed either upward (+1) or downward (-1) to the vertices in order to describe the magnetic moments. At high temperatures, entropy overcomes the interaction between these dipoles and the average magnetization (summation of all spin-vectors) is zero. As the temperature drops, the system reaches a critical point called the "Curie point" where the order parameter, $\phi = \partial h_3 / \partial h_1$, (magnetization) emerges, and increases in value from zero. At low temperatures, the energy drives the interaction between the dipoles resulting in a spontaneous magnetization even in zero magnetic field. For ferromagnets, the ordering field, h_1 , is the magnetic field.

Adapted for fluids, this model becomes the lattice gas model describing condensation. In the lattice gas model, each site is either occupied by a particle (+1) or empty (-1) and particle density minus critical density, $(\rho - \rho_c) / \rho_c$, becomes the

order parameter, ϕ_1 . At the critical point, half of all sites are occupied and half are empty and $\rho_c = 1/2$. In fluids, "zero field" corresponds to the appearance of the difference between the densities of liquid and gas, analogous to the appearance of spontaneous magnetization in the Ising model.

Mathematically, the Ising, or lattice gas, model is a powerful tool to a unified theory of phase transitions, describing different systems using one set of theoretical variables. Table 2 shows the universal theoretical variables associated with scaling theory and their physical meaning for ferromagnets and for liquid-gas systems.

Given the fields, the relevant thermodynamic potential for the lattice gas is the grand thermodynamic potential divided by volume, $\Omega/V = -P$, or negative pressure.

Real Fluids and the Lattice Gas Model. The lattice gas has perfect symmetry with respect to the sign of the order parameter, whereas real fluids approach such symmetry only asymptotically. This symmetry, not be confused with the "internal symmetry" discussed in Section 3.1, describes the liquid-vapor coexistence curve in the (ρ, T) plane and the correlation between the arithmetic mean of the liquid and vapor densities and the critical isochore. To incorporate fluid asymmetry into the scaling theory, in 1970's Mermin and Rehr⁷⁹ and Patashinskii and Pokrovskii⁸⁰ introduced the concept of mixing the independent physical fields into the theoretical scaling fields (see also refs. Wilding *et al.*,⁸¹ Anisimov *et al.*,⁸² and Anisimov *et al.*⁸³). According to their approach, which we will call "incomplete scaling," the independent scaling fields in fluids are linear combinations of chemical potential

and temperature:

$$h_1 = a_1 \Delta \hat{\mu} + a_2 \Delta \hat{T}, \quad h_2 = b_1 \Delta \hat{T} + b_2 \Delta \hat{\mu}, \quad (3.15)$$

while the dependent field $h_3 = c_1 \Delta \hat{P} + c_2 \Delta \hat{T}$. Since any two independent critical amplitudes can be incorporated into the scaling function $f^\pm$, it is convenient to adopt $a_1 = 1$ and $b_1 = 1$; then $c_1 = 1$ while c_2 becomes $-\left(\partial \hat{P} / \partial \hat{T}\right)_{h_1=0}$ taken at the critical point. Therefore, the critical part of the field-dependent thermodynamic potential remains the same as in the lattice gas, since in linear approximation $(P - P_{\text{cxc}}) / \rho_c k_B T_c = \Delta \hat{P} - \left(\partial \hat{P} / \partial \hat{T}\right)_{h_1=0,c} \Delta \hat{T}$. Furthermore, as shown by Anisimov *et al.*,^{82, 83} since in classical thermodynamics the absolute value of entropy is arbitrary, the critical value of entropy can be chosen upon practical convenience. It is seen clearly from the basic thermodynamic relation

$$dP = \rho d\mu + \rho S dT, \quad (3.16)$$

that, if the critical entropy is adopted as $S_c = \rho_c^{-1} (\partial P / \partial T)_{h_1=0,c}$, the coefficient a_2 in Eq. (3.15) vanishes and in linear approximation the chemical potential along the vapor-liquid coexistence does not depend on temperature. However, the curvature of this dependence, determined by the second derivative, is well defined. With this choice of the critical entropy, the mixing term $b_2 \Delta \hat{\mu}$ in "incomplete scaling" becomes also well defined, being in lowest approximation the sole contribution to the vapor-liquid asymmetry in real fluids. In particular, since $\Delta \hat{\rho} = \phi_1 + b_2 \phi_2 = \phi_1 + b_2 \Delta(\hat{\rho} \hat{S})$,

this term explains the non-analytic deviation from the law of rectilinear diameter, the $\left|\Delta\hat{T}\right|^{1-\alpha}$ singularity in the "diameter" of vapor-liquid coexistence curve given by $\hat{\rho}_d = (\rho' + \rho'')/2\rho_c + \dots = 1 + D_1\left|\Delta\hat{T}\right|^{1-\alpha} + D_0\left|\Delta\hat{T}\right| + \dots$. Mapping the asymmetric fluid criticality into the symmetric lattice model is achieved in "incomplete scaling" by a redefinition of the order parameter as $\phi_1 = \Delta\hat{\rho} - b_2\Delta(\hat{\rho}\hat{S})$. In "incomplete scaling" the chemical potential μ (up to the third derivative⁶⁹) is an analytic function of temperature along the vapor-liquid coexistence boundary and along the critical isochore above the critical point ($h_1 = 0$). Like in the lattice gas, the second derivative $(\partial^2\mu/\partial T^2)_{h_1=0} = (d^2\mu/dT^2)_{\text{cxc}}$ remains finite at the critical temperature T_c , while $(\partial^2 P/\partial T^2)_{h_1=0} = (d^2 P/dT^2)_{\text{cxc}}$ diverges proportionally to the isochoric heat capacity $\hat{C}_V$.

At this point we encounter a major conceptual problem with mapping real fluids into the lattice-gas even at the mean-field level. In the mean-field approximation the critical part h_3 of the thermodynamic potential, is represented by Landau expansion (3.9). When $h_1 = \Delta\hat{\mu}$, $h_2 = \Delta\hat{T} + b_2\Delta\hat{\mu}$, and $\phi_1 = \Delta\hat{\rho} - b_2\Delta(\hat{\rho}\hat{S})$, this expansion generates asymmetric terms $\propto b_2\Delta\hat{T}(\Delta\hat{\rho})^3$ and $\propto b_2(\Delta\hat{\rho})^5$. However, in the simplest equation of state that realistically describes fluid phase behavior, the van der Waals equation, the term $\propto \Delta\hat{T}(\Delta\hat{\rho})^3$ is absent, while the term $\propto (\Delta\hat{\rho})^5$ exists. Furthermore, in most classical equations of state, $d\hat{\mu}^2/d\hat{T}^2$ along the liquid-vapor coexistence exhibits a discontinuity directly related to the existence of the independent 5th-order term in Landau expansion. The existence of the independent 5th-order term makes exact mapping of fluids into the lattice-gas model by the conventional mixing of physical fields impossible. This problem was recognized a

long time ago⁶⁷ but was not clearly articulated. On the other hand, a theoretical renormalization-group treatment of the 5th-order term^{84, 85, 86, 87, 88} resulted in the emergence of an independent critical exponent $\theta_5 \simeq 1.3$.⁸⁹ The exponent θ_5 does not exist in symmetric models and is expected to belong exclusively to fluids.

More recently, "incomplete scaling" was challenged by Fisher and his coworkers^{90, 91} who developed a new approach, known as "complete scaling for fluids." They proposed that both $(\partial^2\mu/\partial T^2)_{h_1=0}$ and $(\partial^2 P/\partial T^2)_{h_1=0}$ diverge at the critical point like the isochoric heat capacity. A principle possibility of this effect has been known as the "Yang-Yang anomaly"⁹² and has been a subject of prolonged discussions for decades.⁹³ The major conceptual result of "complete scaling" is that asymmetric fluids can be consistently mapped into the symmetric Ising criticality by appropriate mixing of the physical fields into the scaling fields. A redefinition of the order parameter, suggested by "complete scaling," makes a special renormalization-group treatment of the 5th-order term in the effective Hamiltonian for fluids irrelevant, at least, in practice.

Complete Scaling. "Complete scaling" suggests that all three physical fields $\Delta\hat{\mu}$, $\Delta\hat{T}$, and $\Delta\hat{P}$ are equally mixed into three scaling fields h_1 , h_2 , and h_3 . In linear approximation:

$$h_1 = a_1\Delta\hat{\mu} + a_2\Delta\hat{T} + a_3\Delta\hat{P}, \quad (3.17)$$

$$h_2 = b_1\Delta\hat{T} + b_2\Delta\hat{\mu} + b_3\Delta\hat{P}, \quad (3.18)$$

$$h_3 = c_1\Delta\hat{P} + c_2\Delta\hat{\mu} + c_3\Delta\hat{T}. \quad (3.19)$$

The dependent field h_3 is a homogeneous function of h_1 and h_2 as asymptotically given by Eq. (3.3). Far away from the asymptotic region, or if the phase-coexistence locus $h_1 = 0$ exhibits a strong curvature in terms of the physical fields, the linear approximation might be insufficient and appropriate nonlinear terms should be included.

Physical density-like properties, the molecular density and entropy per unit volume, are given by the thermodynamic relations

$$\hat{\rho} = \left(\frac{\partial \hat{P}}{\partial \hat{\mu}} \right)_{\hat{T}}, \quad \hat{\rho} \hat{S} = \left(\frac{\partial \hat{P}}{\partial \hat{T}} \right)_{\hat{\mu}}. \quad (3.20)$$

Since the coefficients c_1 and c_2 can be absorbed by making the thermodynamic potential h_3 dimensional, as given by Eq. (3.1), while the coefficient $c_3 = \hat{S}_c$, one can obtain by applying Eq. (3.20) to Eqs. (3.17-3.19),

$$\hat{\rho} = \frac{1 + a_1 \phi_1 + b_2 \phi_2}{1 - a_3 \phi_1 - b_3 \phi_2}, \quad (3.21)$$

$$\hat{\rho} \hat{S} = \frac{\hat{S}_c + a_2 \phi_1 + b_1 \phi_2}{1 - a_3 \phi_1 - b_3 \phi_2}. \quad (3.22)$$

One can see that while the scaling field are expressed as linear combinations of the physical fields, the physical densities are non-linear combinations of the scaling densities.

Making "Complete Scaling" Simple. Before we apply complete scaling to describe asymmetry in fluids, we note that the relations between scaling and physical fields

can be further simplified. The coefficients a_1 and b_1 can be absorbed by the two amplitudes in the scaling function $f^\pm$, such that $a_1 = 1$ and $b_1 = 1$. The coefficient $c_3 = \hat{S}_c$ is determined by the choice of the critical value of entropy. By adopting $\hat{S}_c = (k_B \rho_c)^{-1} (\partial P / \partial T)_{h_1=0,c} = \left(d\hat{P} / d\hat{T} \right)_{\text{cxc},c}$, the slope of the saturation-pressure curve at the critical point, one obtains $a_2 = -a_3 \left(d\hat{P} / d\hat{T} \right)_{\text{cxc},c}$. Indeed, along the path $h_1 = 0$, asymptotically close to the critical point,

$$\left(\frac{\partial \hat{\mu}}{\partial \hat{T}} \right)_{h_1=0,c} + a_2 + a_3 \left(\frac{\partial \hat{P}}{\partial \hat{T}} \right)_{h_1=0,c} = 0. \quad (3.23)$$

On the other hand, it follows from the thermodynamic relation (3.16) that

$$\frac{d\hat{\mu}}{d\hat{T}} + \hat{S}_c - \frac{\partial \hat{P}}{\partial \hat{T}} = 0. \quad (3.24)$$

Thus, with adopting $\hat{S}_c = \left(\partial \hat{P} / \partial \hat{T} \right)_{h_1=0,c}$, we obtain $\left(\partial \hat{\mu} / \partial \hat{T} \right)_{h_1=0,c} = 0$ and

$$a_2 + a_3 \left(\frac{\partial \hat{P}}{\partial \hat{T}} \right)_{h_1=0,c} = 0. \quad (3.25)$$

Furthermore, with such a choice of $\hat{S}_c$, along the path $h_1 = 0$

$$h_2 = \Delta \hat{T} \left(1 - b_3 \frac{a_2}{a_3} \right), \quad (3.26)$$

and the density of entropy becomes proportional to the weakly-fluctuating scaling density, $\Delta(\hat{\rho} \hat{S}) \approx (1 + b_3) \phi_2 \propto |h_2|^{1-\alpha}$. With exception for a trivial renormalization of the amplitudes in h_2 and $\Delta(\hat{\rho} \hat{S})$, the coefficient b_3 plays no significant role in

asymmetry of fluid criticality. Indeed, as follows from Eqs. (3.21) and (3.22), this coefficient can be independently obtained only from the contributions to the density behavior of order $b_3\phi_1\phi_2 \propto |h_2|^{1-\alpha+\beta}$. With $1 - \alpha + \beta \simeq 1.417$, this contribution is of higher order than $a_3\phi_1^2 \propto |h_2|^{2\beta}$ and $b_2\phi_2 \propto |h_2|^{1-\alpha}$, and even significantly weaker than the linear term. Therefore, for the sake of simplicity, we assume $b_3 = 0$. Hence, there are only two independent coefficients that in the first approximation control the asymmetry in fluid criticality, namely a_3 and b_2 . In this approximation, the scaling fields read

$$h_1 = \Delta\hat{\mu} + a_3 \left[\Delta\hat{P} - \left(d\hat{P}/d\hat{T} \right)_{\text{cxc,c}} \Delta\hat{T} \right], \quad (3.27)$$

$$h_2 = \Delta\hat{T} + b_2\Delta\hat{\mu}, \quad (3.28)$$

$$h_3 = \Delta\hat{P} - \Delta\hat{\mu} + \left(d\hat{P}/d\hat{T} \right)_{\text{cxc,c}} \Delta\hat{T}. \quad (3.29)$$

Furthermore, by expanding Eqs. (3.21) and (3.22) and neglecting all terms of higher-order than linear of $\Delta\hat{T}$, we obtain

$$\Delta\hat{\rho} \simeq (1 + a_3)\phi_1 + a_3(1 + a_3)\phi_1^2 + b_2\phi_2 \quad (3.30)$$

$$\Delta(\hat{\rho}\hat{S}) \simeq b_2\phi_2 \quad (3.31)$$

As a result, while the order parameter in fluids is, in general, a nonlinear combination of density and entropy, the weakly fluctuating scaling density ϕ_2 in first approximation is associated with the density of entropy only.

The relations between the theoretical fields and the physical fields given by Eqs. (3.27-3.29) are to be built into a theoretical equation of state based on the scaling formulation given by Eq. (3.3).

CHAPTER 4

APPLYING CRITICAL POINT UNIVERSALITY TO SUPERCOOLED LIQUID WATER

The application of the principle of critical point universality to supercooled liquid water provides an opportunity to explore the second critical point scenario from a new direction. Since conclusive experimental evidence supporting one of the three proposed interpretations of existing data is not available, the role of theoretical models in supporting these theories has grown. Yet Monte Carlo and molecular dynamic simulations are still only approximate models of water's complex molecular bonding interactions and they depend heavily on the accuracy of many underlying assumptions.¹ An equation of state, developed under the assumption of the existence of the second critical point and based on the principle of critical point universality, offers a thermodynamically consistent approach to explore the behavior of supercooled liquid water. Using only two adjustable critical parameters, a system-dependent critical amplitude and the critical pressure, and an adjustable non-critical background, we can locate the second critical point in liquid water and predict thermodynamic properties. The comparison between existing experimental data and the predicted behavior of the thermodynamic properties will offer a new tool to evaluate the validity of the second critical point scenario.

4.1 Relations Between Theoretical and Physical Fields

The first step in the development of the equation of state is to map the theoretical scaling fields to physical variables. Representation of scaling fields through

linear mixing of physical fields is used to incorporate asymmetric fluid criticality into the symmetric Ising model.^{94, 95} We begin with the "complete scaling" relations, Eqs. (3.17-3.19). The degree of freedom of the system requires only two independent variables. Therefore, all but two coefficients in the scaling fields may be absorbed in the two system-dependent amplitudes of the scaling function f . In this model, we adopt the mixing coefficients, $a_2 = 1$, $b_2 = -1$, $c_1 = -1$, $c_2 = 1$, $c_3 = \hat{S}_c$, and simplify the equations:

$$h_1 = a_1 \Delta \hat{\mu} + \Delta \hat{T} + a_3 \Delta \hat{P}, \quad (4.1)$$

$$h_2 = b_1 \Delta \hat{T} - \Delta \hat{\mu} + b_3 \Delta \hat{P}, \quad (4.2)$$

$$h_3 = -\Delta \hat{P} + \Delta \hat{\mu} + \hat{S}_c \Delta \hat{T}. \quad (4.3)$$

Such a choice anticipates the fact that the coefficients a_1 , b_1 , a_3 , and b_3 can be very small, since the supercooled water is weakly compressible. The negative sign of $b_2 = -1$ indicates that the liquid-liquid phase separation in supercooled water occurs with an increase of pressure (Fig. 1), in contrast to the vapor-liquid phase separation. Moreover, since the compressibility of supercooled water is very small, we assume a_3 and b_3 are small enough so that they can be neglected for the purposes of our model. The value of a_1 and b_1 can be determined from the shape of the liquid-

liquid first-order transition curve. Finally,

$$h_1 = a_1 \Delta\mu + \Delta T, \quad (4.4)$$

$$h_2 = b_1 \Delta T - \Delta\mu, \quad (4.5)$$

$$h_3 = -\Delta P + \Delta\mu. \quad (4.6)$$

In order to further simplify the fields, we must adopt a critical value of $\hat{S}_c$. For the vapor-liquid critical point, the convenient choice for $\hat{S}_c$ was $(k_B \rho_c)^{-1} (\partial P / \partial T)_{h_1=0,c}$. However, the liquid-liquid coexistence curve in supercooled water has a very different slope than the liquid-gas coexistence curve (Fig. 12) and in the case of liquid-liquid coexistence it becomes convenient to rotate the theoretical coordinates h_1 and h_2 through a different choice for critical entropy. Adopting a critical entropy of $\hat{S}_c = 0$ with $a_3 \approx 0$ and $b_3 \approx 0$, results in

$$\left(\frac{\partial \hat{\mu}}{\partial \hat{T}} \right)_{h_1=0,c} = \frac{1}{\hat{\rho}} \left(\frac{\partial \hat{P}}{\partial \hat{T}} \right)_{h_1=0,c} = -\frac{a_2}{a_1}, \quad (4.7)$$

$$\left(\frac{\partial \hat{\mu}}{\partial \hat{T}} \right)_{h_2=0,c} = \frac{1}{\hat{\rho}} \left(\frac{\partial \hat{P}}{\partial \hat{T}} \right)_{h_2=0,c} = -\frac{b_1}{b_2} \quad (4.8)$$

along the paths $h_1 = 0$ or $h_2 = 0$, asymptotically close to the critical point. In this approximation, the scaling fields h_1 and h_2 read

$$h_1 \simeq a_1 \Delta \hat{\mu} + a_2 \Delta \hat{T} = a_1 \Delta \hat{\mu} - \frac{a_1}{\hat{\rho}} \left(\partial \hat{P} / \partial \hat{T} \right)_{h_1=0,c} \Delta \hat{T}, \quad (4.9)$$

$$h_2 \simeq b_1 \Delta \hat{T} + b_2 \Delta \hat{\mu} = b_1 \Delta \hat{T} + \frac{b_1}{\hat{\rho}} \left(\partial \hat{P} / \partial \hat{T} \right)_{h_1=0,c} \Delta \hat{\mu}. \quad (4.10)$$

Solving these equations for the scaling densities yields

$$\phi_1 = - \left(\frac{\partial \Delta h_3}{\partial h_1} \right)_{h_2} = \frac{\Delta (\hat{\rho} \hat{S}) + b_1 \Delta \hat{\rho}}{1 + a_1 b_1} \approx \hat{B}_0 |h_2|^\beta, \quad (4.11)$$

$$\phi_2 = - \left(\frac{\partial \Delta h_3}{\partial h_2} \right)_{h_1} = \frac{\Delta \hat{\rho} + a_1 \Delta (\hat{\rho} \hat{S})}{1 + a_1 b_1} \approx \frac{\hat{A}_0}{1 - \alpha} |h_2|^{1-\alpha}. \quad (4.12)$$

If b_1 is small, the predominant contribution to the order parameter, ϕ_1 , comes from the entropy. If a_1 is small, the second scaling density becomes mostly molecular density.

In addition to the difference in direction of the slope of the liquid-liquid transition line, defined as $h_1 = 0$, the liquid-liquid transition also curves strongly above the critical point. To account for this curvature, we added the non-linear pressure term, $a_3 \Delta \hat{\mu}^2$, in the ordering field, h_1 , and our scaling fields become:

$$h_1 = a_1 \Delta \hat{\mu} + a_2 \Delta \hat{T} + a_3 \Delta \hat{\mu}^2 = a_1 \Delta \hat{\mu} - a_1 \left(\partial \hat{P} / \partial \hat{T} \right)_{h_1=0,c} \Delta \hat{T} + a_3 \Delta \hat{\mu}^2 \quad (4.13)$$

$$h_2 = b_1 \Delta \hat{T} + b_2 \Delta \hat{\mu} = b_1 \Delta \hat{T} + b_1 \left(\partial \hat{P} / \partial \hat{T} \right)_{h_1=0,c} \Delta \hat{\mu}. \quad (4.14)$$

Finally, the scaling fields, "ordering" and "thermal," for the liquid-liquid critical point in supercooled water become

$$h_1 \simeq \Delta \hat{T} - \left(\partial \hat{T} / \partial \hat{P} \right)_{h_1=0,c} \hat{\rho}^{-1} \Delta \hat{P} - 2 \left(\partial^2 \hat{T} / \partial \hat{P}^2 \right)_{h_1=0,c} \hat{\rho}^{-2} \left(\Delta \hat{P} \right)^2, \quad (4.15)$$

$$h_2 \simeq -\hat{\rho}^{-1} \Delta \hat{P} - \left(\partial \hat{T} / \partial \hat{P} \right)_{h_1=0,c} \Delta \hat{T}. \quad (4.16)$$

The scaling “densities” become

$$\phi_1 \simeq \frac{\Delta \left(\hat{\rho} \hat{S} \right) + b_1 \Delta \hat{\rho}}{1 + (a_1)_{\text{eff}} b_1}, \quad (4.17)$$

$$\phi_2 \simeq \frac{\Delta \hat{\rho} + (a_1)_{\text{eff}} \Delta \left(\hat{\rho} \hat{S} \right)}{1 + (a_1)_{\text{eff}} b_1}. \quad (4.18)$$

where $\Delta \hat{S} \equiv (S - S_c)/R$, with R being the gas constant, and $(a_1)_{\text{eff}} = \left(\partial h_1 / \partial \hat{P} \right)_{\hat{T}} = a_1 + 2a_3 \Delta \hat{P}$. The "strong," "weak," and "cross" susceptibilities remain defined as

$$\chi_1 = \left(\frac{\partial \phi_1}{\partial h_1} \right)_{h_2}, \quad (4.19)$$

$$\chi_2 = \left(\frac{\partial \phi_2}{\partial h_2} \right)_{h_1}, \quad (4.20)$$

$$\chi_{12} = \chi_{21} = \left(\frac{\partial \phi_1}{\partial h_2} \right)_{h_1} = \left(\frac{\partial \phi_2}{\partial h_1} \right)_{h_2}, \quad (4.21)$$

As far as the physical fields are mixed into the scaling fields, the physical properties, such as the isobaric heat capacity C_P , the isothermal compressibility κ_T , and the thermal expansivity α_P , will not exhibit universal power laws when measured along isotherms or isobars; instead, their apparent behavior will be determined by a thermodynamic path and by the values of the mixing coefficients in Eqs. (2) and (3). As follows from Eqs. (4.15) and (4.16), the critical (fluctuation induced) parts of the dimensionless isobaric heat capacity, isothermal compressibility, and thermal

expansivity are expressed through the scaling susceptibilities as

$$\left(\hat{C}_P\right)_{\text{cr}} = \hat{T} \left(\frac{\partial \hat{S}}{\partial \hat{T}} \right)_{\hat{P}} - \left(\hat{C}_P\right)_{\text{b}} \quad (4.22)$$

$$\begin{aligned} &= \hat{T} \left(a_2^2 \chi_1 + 2a_2 b_1 \chi_{12} + b_1^2 \chi_2 \right), \\ \left(\hat{\kappa}_T\right)_{\text{cr}} &= -\frac{1}{\hat{V}} \left(\frac{\partial \hat{V}}{\partial \hat{P}} \right)_{\hat{T}} - \left(\hat{\kappa}_T\right)_{\text{b}} \end{aligned} \quad (4.23)$$

$$\begin{aligned} &= \frac{1}{\hat{V}} \left((a_1)_{\text{eff}}^2 \chi_1 + 2(a_1)_{\text{eff}} b_2 \chi_{12} + b_2^2 \chi_2 \right), \\ \left(\hat{\alpha}_P\right)_{\text{cr}} &= \frac{1}{\hat{V}} \left(\frac{\partial \hat{V}}{\partial \hat{T}} \right)_{\hat{P}} - \left(\hat{\alpha}_P\right)_{\text{b}} \end{aligned} \quad (4.24)$$

$$= -\frac{1}{\hat{V}} \left((a_1)_{\text{eff}} a_2 \chi_1 + ((a_1)_{\text{eff}} b_1 + a_2 b_2) \chi_{12} + b_1 b_2 \chi_2 \right).$$

where $\hat{T} = T/T_c$, $\hat{P} = P/\rho_c R T_c$, and the subscript "b" indicates the property backgrounds, behavior not attributable to proximity of the critical point. Given the small slope of the liquid-liquid coexistence curve in the (P, T) plane, the mixing coefficients a_1 and b_1 are small (Fig. 16). We can see that the thermodynamic properties depend on susceptibilities such that $\hat{C}_P$ is strongly divergent, $\hat{\kappa}_T$ is mostly weakly divergent, and $\hat{\alpha}_P$ is mostly modestly divergent. In practical ranges of temperatures and pressures, roughly,

$$\hat{C}_P \propto \chi_1, \quad (4.25)$$

$$\hat{\kappa}_T \propto \chi_1, \quad (4.26)$$

$$\hat{\alpha}_P \propto \chi_{12}. \quad (4.27)$$

The application of scaling theory to the liquid-liquid critical point in super-

cooled water is not a unique result, but it does differ from the liquid-vapor or even binary system liquid-liquid translations of the theoretical variables to physical variables. Liquid crystals such as Blue Phase III have a critical point of the transition between a molecular-fluid phase and a structural phase that translates into scaling theory in a similar manner to the liquid-liquid critical point in supercooled water.⁹⁵ For the blue phase liquid crystal the phase BPI, the defect lies (disclinations) of a helix structure form simple cubic lattice. For the phase BP II, the defects form a body centered cubic lattice. In BP III, defects form an amorphous structure with a translation between a "liquid" of defects (BP III) and a "gas" of defects ("molecular fluid"). Like in supercooled water, the transition temperature is almost independent of the second-physical field. A cartoon analogy between the liquid-vapor and liquid-liquid critical points is given in Table 3.

4.2 Scaled Parametric Equation of State

The universal scaling function and renormalization group theory allow calculation of the singular parts of all thermodynamic properties of a fluid in the asymptotic vicinity of the critical point given the critical parameters, any two system-dependent scaling critical amplitudes, and the proportional slope of the coexistence curve at the critical point. However, the expressions for the scaling function are implicit and inconvenient for practical engineering use. The phenomenological parametric representations of a scaled equation of state provide more convenient coordinates using the parametric variables r and θ , where r measures the distance from the critical point and θ provides a location along a contour of constant r .

We use the simplest form of a scaled parametric equation of state, the so-called "linear model," which represents the scaling fields and scaling susceptibilities as functions of the "polar" variables r and θ ^{95, 69}:

$$h_1 = ar^{\beta+\gamma}\theta(1-\theta^2), \quad (4.28)$$

$$h_2 = r(1-b^2\theta^2), \quad (4.29)$$

$$\chi_1 = \frac{k}{a}r^{-\gamma}c_1(\theta),$$

$$\chi_{12} = kr^{\beta-1}c_{12}(\theta), \quad (4.30)$$

$$\chi_2 = akr^{-\alpha}c_2(\theta) - B_{\text{cr}} \quad (4.31)$$

where the coefficient $b^2 = (\gamma - 2\beta) / \gamma(1 - \beta) \simeq 1.36$ is a universal constant, while a and k are system-dependent amplitudes, and B_{cr} is the so-called "critical background" of order ak .⁹⁵ The critical background was studied by Bagnuls and Bervillier in a three-dimensional field theory⁹⁶ and by Anisimov *et al.* in a crossover theory based on a renormalized Landau expansion.⁹⁷ According to the theory, the critical background can be found through an explicit equation proportional to the cutoff wave number of the critical fluctuations. Unfortunately, the available data are accurate enough to estimate B_{cr} through this theory for only a few fluids such as methane⁹⁸ and ethane⁹⁹ in the two-phase region. Although critical background is a difficult parameter to obtain accurately, it can be estimated to an order of magnitude as $B_{\text{cr}} \approx ak$. The analytical functions $c_1(\theta)$, $c_2(\theta)$, and $c_{12}(\theta)$ are calculated in ref..⁹⁵ The remarkable feature of the "linear model" is that the singularities in

the thermodynamic functions are only related to the variable r , while the properties are analytical with respect to θ . The parameter θ is chosen to range from -1 to +1 so that $\theta = 0$ corresponds with the critical isochore and $\theta = \pm 1$ corresponds to the coexistence curve. Along the critical isotherm, $h_2 = 0$, the value of theta becomes $\theta = \pm 1/b$. Figure 16 shows the representation of the thermal field h_2 and the order parameter ϕ_1 through the variables of the parametric linear model.

Input Parameters for the Scaled Parametric Equation of State. The choice of a coordinate system, reference entropy, and morphology of the liquid-liquid coexistence curve correlated the universal scaling theory to the physical variables specific to the scaled parametric equation of state for a liquid-liquid critical point in supercooled water. Until this point, the equation of state remains applicable for both ordinary and heavy water and the translation from theoretical variables to physical variables did not introduce any sources of error. However, this scaled equation of state depends on input parameters: density of water at various pressures, the path of the coexistence curve and its extension into the one-phase region, the location of the critical point along that curve, and the system-dependent amplitudes a and k . Each of these parameters introduces error into the equation of state.

Density. The International Association for the Properties of Water and Steam (IAPWS) provides accepted formulations for the properties of water for scientific and industrial applications. In 1995, IAPWS approved a new formulation of the properties for water for general and scientific use based on existing experimental

data. This formulation, serving as the international standard for water's thermodynamic properties, provides the density of water at various pressures and temperatures. In the stable liquid region at ambient pressure, IAPWS-95 is accurate to $\leq \pm 0.0001\%$ and represents the most accurate data within the experimental uncertainty available. However, the formulation covers a validity range from 251.2K at 209.9 MPa to 1273 K and 1000MPa, while our equation of state suggests a critical point in supercooled liquid water below 250K and 50MPa. Nevertheless, the IAPWS formulation represents the most accurate, available data on the density of liquid water and the scaled parametric equation of state depends on the IAPWS-95 predicted density values at various temperatures and pressures. Fig. 17 shows plots of the IAPWS density for various pressures and temperatures.

The formulation used for ordinary water is presented in ref.³ The formulation used for heavy water is a dimensionless version of the formulation provided by Hill *et al.*^{100, 101} IAPWS released a Revised Release on the IAPWS formulation for heavy water in July 2005.

Coexistence Curve and "Widom line." The "Widom line" in the one-phase region, $h_1 = 0$, is an analytical continuation of the liquid-liquid transition curve from C' to lower pressures and higher temperatures. Based on the most recent estimate of the liquid-liquid phase transition curve given by Mishima,⁶² we have obtained the coefficients $a_1 = b_1 = 0.039$ and $a_3 = 0.062$ for ordinary water and $a_1 = b_1 = 0.03$ and $a_3 = 0.05$ for heavy water. This work shows the location of the liquid-liquid transition line close to the homogeneous ice nucleation locus. Fitting a curve to

the estimates of Mishima allows us to specify the location of the critical point with only one variable, P_c , reducing the number of variables, and inherent error, in our equation. Figure 18 shows a plot of the liquid-liquid coexistence curve based on Mishima data for ordinary and heavy water.

System-Dependent Amplitudes. In order to reduce the number of adjustable parameters, we assume that the ratio $k/a = 1$, as obtained for the three dimensional Ising model with short-range interactions.¹⁰² Hence, only two adjustable parameters, namely, P_c and $a = k$, have been used to describe the anomalous parts of the thermodynamic properties.

Adjustable Parameters $a = k$, and P_c . Using high-resolution experimental heat-capacity data¹² shown in Fig. 4, we optimized the location of the critical point and the system dependent amplitudes. The resulting fit for the experimental heat capacity data is shown in Figure 19. The non-critical background of the heat capacity was approximated as a linear function of temperature. We obtained $a = k = 0.47$ and $P_c = 27$ MPa with the critical temperature corresponding to this pressure $T_c = 232$ K for ordinary water. For heavy water, we fixed $a = k = 0.7$ and $P_c = 20$ MPa with the critical temperature corresponding to this pressure $T_c = 238$ K. The critical point, obtained from our equation of state, is located at a much lower pressure than previously predicted from computer simulations (see Fig. 13). Figure 20 shows the parametric equation of state predicted by scaling theory.

Non-critical Background. The scaled parametric equation of state predicts the effect of the critical point on the behavior of thermodynamic properties, which dominates in the immediate vicinity of the critical point. However, the available experimental data are usually taken far away from the critical point where classical thermodynamic behavior becomes predominate. There are several approaches to dealing with the crossover to classical thermodynamic behavior and for this work we use a simple polynomial, which grows with distance from the critical point. The backgrounds for the parameters are given in Table 4.

CHAPTER 5

PREDICTING THERMODYNAMIC PROPERTIES OF SUPERCOOLED LIQUID WATER

With the given amplitudes and location of the critical point, obtained from the heat capacity data as shown in Chapter 4, we predict the behavior of the compressibility and expansivity, shown in Figs. 21 and 22, by adjusting only their non-critical backgrounds. Similar predictions were performed for heavy water, shown in Figs. 23 and 24. The predictions appear to have excellent agreement with the experimental data.^{14, 15} While it is difficult to establish the error bars for the obtained P_c value, the parametric equation of state certainly excludes the critical pressure above 50 MPa or below 10 MPa for ordinary water and values of above 40MPa and below 5MPa for heavy water.

A Lower Pressure for the Second Critical Point. The location of the critical point, far lower than previously predicted, has some additional experimental support. Mishima melted various heavy water ice and measured the onset of the change in sample temperature during the decompression-induced melting experiment. In heavy water ice V, IV and XIII there appeared to be a sharp change in slope that suggests the possibility of the HDL to LDL transition line. However, in heavy water ice III, the line curved smoothly. Figure 25 shows experimental results and a schematic representation with the second-critical point. These data suggest a critical point for heavy water below 60 MPa and above 10 MPa, consistent with the predictions in this thesis.

Scaling versus Mean-Field Predictions. We also conclude that the mean-field scenario is unlikely. The mean-field scenario cannot predict the anomalous behavior of isothermal compressibility within our model. While the major contribution in the heat-capacity anomaly is strong susceptibility, χ_1 , (b_1 is small) diverging both in mean-field and in scaling theory, the major contribution in the isothermal compressibility anomaly is the weak susceptibility χ_2 , (a_1 is small) which shows no anomaly in mean-field approximation. The major contribution in the critical part of the expansivity comes from the cross susceptibility χ_{12} as both a_1 and b_1 are small. These features make the second critical point in water essentially different from the liquid-vapor critical point where C_P , κ_T , and α_P all diverge strongly, as χ_1 , and from the liquid-liquid critical points in binary fluids where C_P , κ_T , and α_P all diverge weakly, as χ_2 .

Limitations to the Scaled Equation of State. There are obvious limitations of our equation of state. First, the model used in this work is accurate only asymptotically close to the critical point ($r \ll 1$) while all measurements in supercooled water have been taken far beyond the asymptotic region. The experimental range of r , the parametric distance to the critical point, at worst may be as large as 0.5. However, this is the first estimate of the critical parameters for the second critical point in water based on experimental data, and not on computer simulations of "water like" models. Including non-asymptotic corrections to the parametric equation of state would change the adjustable backgrounds while not significantly affecting the critical parameters. To more accurately describe and predict the properties in a broader

range of pressures and densities in supercooled water, a “global” crossover equation of state,⁶⁹ based on a reliable mean-field equation of state, such as a modified van der Waals model,⁶⁰ is required. Moreover, we did not address an intriguing possibility of the existence of multiple critical points in supercooled water, as predicted by some simulated water models.^{103, 104}

In this work, the order parameter is phenomenologically expressed through molar volume and entropy, with entropy being the major contribution. A clarification of the relation between this phenomenology and the microscopic nature of the order parameter⁵¹ would help in better understanding the physics of phase transitions in supercooled water.

Nature of the Order Parameter. In supercooled liquid water, the nature of the order parameter is not associated mostly with density, as is the case of the liquid-vapor critical point. Studies by Poole *et al.*⁶⁰ and Truskett *et al.*⁵¹ have looked at the connection between the theoretical, microscopically defined order parameter, $(\phi_1)_{theoretical} = (B_0)_{theoretical} |h_2|^\beta$, and the physical fields, while the phenomenologically defined order parameter is:

$$\phi_1 = \frac{\Delta(\hat{\rho}\hat{S}) + b_1\Delta\hat{\rho}}{1 + a_1b_1} \approx B_0 |h_2|^\beta. \quad (5.1)$$

Poole’s and Truskett’s scalar order parameter is related to an optimal orientation of hydrogen bonds. The microscopically defined order parameter belongs to the Ising universality class and linearly couples with entropy and density, unlike in fluids,

while dynamically, it may belong to a dynamic universality class of non-conserved order parameter.

Hajime Tanaka also explored the nature of the order parameter, suggesting the possibility of a two-order-parameter description and introduced a bond order parameter defined as the local fraction of locally favored structures.¹⁰⁶

Other Equations of State. Kiselev and Ely^{107, 108} were the first to apply fluctuation theory to supercooled water and calculate the physical properties of ordinary and heavy water. Their work encompassed predictions of the thermodynamic properties of ordinary water, heavy water and ordinary and heavy water mixtures, as well as the development of a crossover equation of state. However, in order to predict properties in both the supercooled and the stable regions and provide reasonable values for heavy water, ordinary water and mixtures, Kiselev and Ely incorporated over a dozen system-dependent parameters into their equation of state. The resulting predictions were more empirical than fundamental. Moreover, the predicted phase diagram looks unrealistic with the (P, T) slope positive instead of negative, as well established. The scaled parametric equation of state developed in this thesis is more limited in scope, but relies on only three adjustable parameters, the critical pressure P_c , the system dependent amplitude k/a , and the non-critical backgrounds.

Multiple Critical Points. The predictions of the scaled, parametric equation of state support the hypothesis of a second critical point in supercooled water. However, this result does not preclude the possibility of multiple critical points. Molecular dynamic models and monte carlo simulations, such as those of Brovchenko *et*

al. show four possible phases of supercooled liquid water, corresponding with observed densities in amorphous ice.¹⁰⁹ The debate regarding the number of phases of amorphous ice experimentally observed and the level of uncertainty built into the equation of state support further exploration of the multiple critical points in supercooled liquid water.

CHAPTER 6

SUMMARY

The scaled equation of state for supercooled liquid water offers a consistent scaling description of the available experimental data in supercooled water. Although this work is not absolutely definitive in its support of the second-critical-point scenario, it lends weight to a growing body of evidence and provides another tool for future evaluations as additional experimental data become available.

This work represents one piece of a much larger puzzle in the development of a thermodynamically consistent equation of state for liquid water in general. When complete, the implications for this work are widespread. Supercooled liquid water occurs naturally in the atmosphere, playing a role in weather and global warming by absorbing solar and terrestrial energy changes. The high pressures and low temperatures necessary for supercooled liquid water also occur naturally on some of our neighboring planets. Storms on Mars and photos of Europa, Jupiter's moon, suggest the presence of supercooled liquid water. Aqueous solutions also represent the importance of supercooled liquid water. The phase behavior of pure liquid water shifts when put in solution, potentially either shifting the phenomena previously only seen in deep supercooled regions into an area of the phase diagram more accessible at ambient temperatures and pressures or making the states of the solution stable at temperatures below 0°C. Aqueous solutions below 0°C have implications for deep ocean science, underwater communication and navigation as well as biological systems. In addition, an understanding of the behavior of liquid

water might provide insight into polyamorphism in phosphorous,^{110, 111} and other substances, such as SiO_2 , and GeO_2 , which exhibit similar anomalous behavior upon cooling.^{112, 113}

APPENDIX I: TABLES

Thermodynamic Property	Formula	Path	Classical Critical Exponent	Non-classical Critical Exponent
Isothermal Compressibility	$\kappa_T \approx \Gamma_0^\pm (\Delta\hat{T})^{-\gamma}$	$\rho = \rho_c$	1	1.239 ± 0.002
Isochoric Heat Capacity	$C_V \approx A_0^\pm (\Delta\hat{T})^{-\alpha}$	$\rho = \rho_c$	0	0.110 ± 0.003
Density	$\rho - \rho_c \approx \pm B_0 (-\Delta\hat{T})^\beta$	Coexistence $\mu_1 = \mu_2$	$\frac{1}{2}$	0.326 ± 0.002
Pressure	$P - P_c \approx (\Delta\hat{p})^\delta$	$T = T_c$	3	4.8 ± 0.02
Correlation Function, $G(r)$	$G(r) \approx r^{-(1-\eta)}$	Critical point; large r	0	0.031 ± 0.004
Correlation Length, ξ	$\xi \approx \xi_0^\pm (\Delta\hat{T})^{-\nu}$	$\rho = \rho_c$	$\frac{1}{2}$	0.063 ± 0.001

Table 1. Classical and Non-classical Critical Exponents. $A_0^\pm, B_0^\pm, \Gamma_0^\pm, \xi_0^\pm$ are critical amplitudes above and below the critical temperature.

Universal Variables	Ising (ferromagnets)	Lattice Gas (liquid-gas)
h_1	Magnetic Field	$\Delta\hat{\mu} = (\mu - \mu_c) / RT_c$
h_2	$\Delta\hat{T}$	$\Delta\hat{T}$
ϕ_1	Magnetization	$\Delta\hat{\rho}$
ϕ_2	$\Delta\hat{S} = \Delta S / k_B$	$\Delta(\hat{\rho}\hat{S}) = (\rho S - \rho_c S_c) / r_c k_B$

Table 2. Scaling theory universal theoretical variables for ferromagnets and liquid-gas systems.

Symbol	Variable	Liquid-Vapor	Liquid-Liquid (dT/dm)	Liquid-Liquid (binary liquid)
			(water, BPIII)	
ϕ_1	Order parameter	$\Delta\rho$	ΔS	Δx
h_1	Ordering field	$\Delta\mu$	ΔT	$\Delta\mu_{21}$
h_2	“Thermal” scaling field	ΔT	$\Delta\mu$	ΔT
ϕ_2		$\Delta(\rho S)$	$\Delta\rho$	ΔS
χ_1	Strong susceptibility	$\kappa_T \quad \alpha_P \quad C_P$	C_P	$\partial x / \partial \mu_{21}$
χ_2	Weak susceptibility	C_V	κ_T	$\kappa_T \quad \alpha_P \quad C_P$
χ_{12}	Cross susceptibility	$(\partial\rho / \partial T)_{h_1=0}$	α_P	$(\partial x / \partial T)_{h_1=0}$

Table 3. Cartoon analogy between liquid-vapor and liquid-liquid critical points.

Thermodynamic Property	Non-critical Background
C_p (0.1 MPa)	$7.8 * \Delta T + 2.1$
κ_T (0.1 MPa)	0.000456
κ_T (10 MPa)	0.000456
κ_T (50 MPa)	$0.00005 * \Delta T + 0.00039$
κ_T (100 MPa)	$-0.00034 * \Delta T + 0.000436$
κ_T (150 MPa)	$-0.000326 * \Delta T + 0.000396$
κ_T (190 MPa)	$-0.00024 * \Delta T + 0.00034$
α_T (0.1 MPa)	$0.00125 * \ln(1.77297 * \Delta T^{1.05498}) + 0.002 - 0.0122 * \Delta T + 0.017 * \Delta T^2 - (0.00085 * \ln(0.18418 * \Delta T^{0.33789}))$
C_p (0.1 MPa)	$2.3 * \Delta T + 8.5$
κ_T (10 MPa)	$-0.178 - 0.00974 * T + 5.5E - 5 * T^2 - 1.364E - 7 * T^3 + 1.257E - 10 * T^4$
κ_T (50 MPa)	$0.00035 * \Delta T + 0.00033$
κ_T (100 MPa)	$-0.0006 * \Delta T + 0.00053$
κ_T (150 MPa)	$-0.00042 * \Delta T + 0.00047$
κ_T (190 MPa)	$-0.00024 * \Delta T + 0.00039$
α_T (0.1 MPa)	$0.0000000000000014 * \Delta T^4 - 0.0000043 * \Delta T + 0.0023$

Table 4. Non-critical background polynomials for ordinary water (aqua blue) and heavy water (sky blue).

APPENDIX II: FIGURES

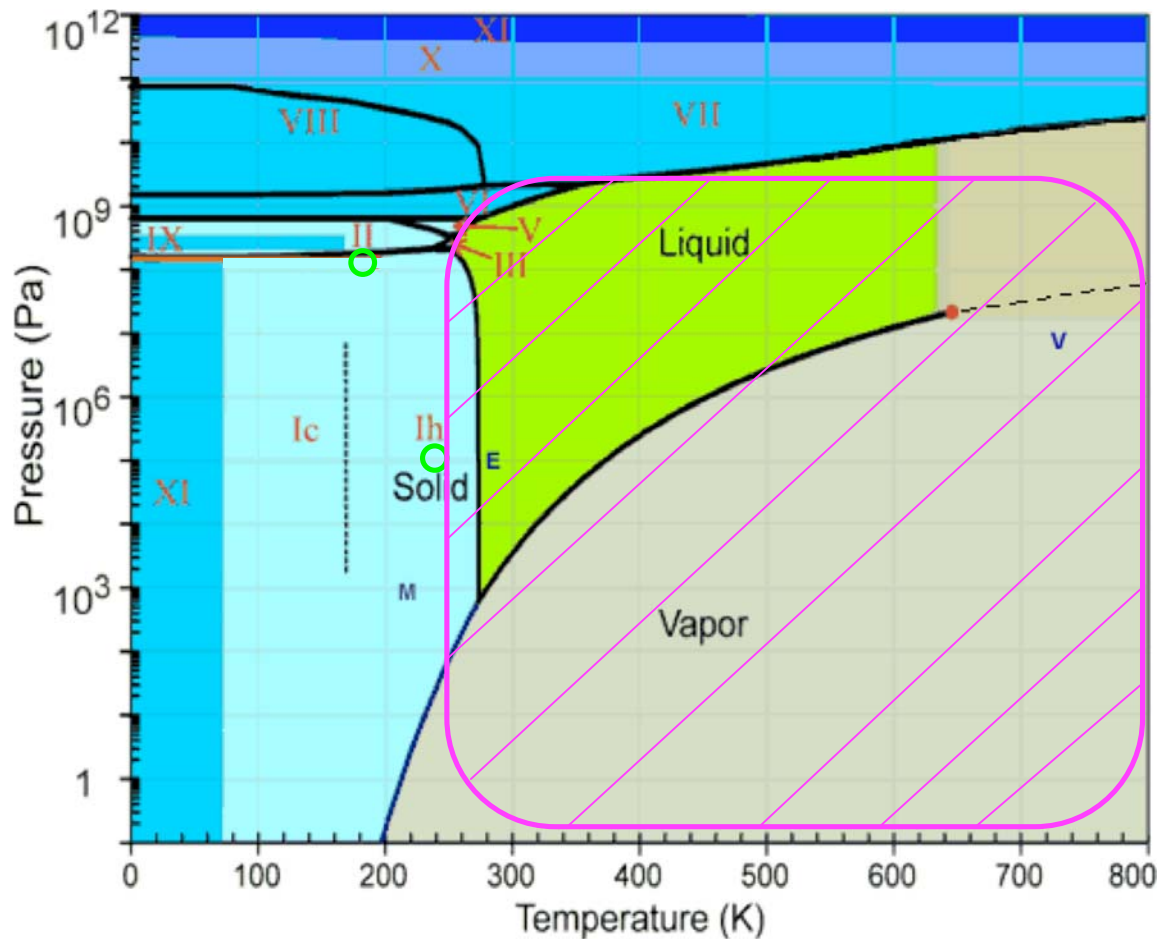


Figure 1. Phase diagram of water showing stable regions of vapor, liquid, and various forms of ice. The region inside the purple curve shows the range of validity for the IAPWS-95 empirical equation of state. IAPWS-95 is recommended by the International Association for the Properties of Water and Steam (IAPWS) for general and scientific use. Developed to accurately reproduce thermodynamic properties in the stable range, the IAPWS-95 formulation for liquid water is valid for temperatures ranging from 240K in the metastable region to 1273 K, and for positive pressures up to 1000MPa.^{3,4} The IAPWS-95 region of validity is shown as a shaded box, . Kanno *et al.*¹⁶ cooled liquid water down to -38°C at 0.1 MPa and down to -92°C at 200 MPa. The limits of experiments from Kanno *et al.* are shown as green circles, ○. Figure adapted from London South Bank University webpage <http://www.lsbu.ac.uk/water/phase.html>, and reprinted with permission from Dr. Martin Chaplin.¹¹⁴

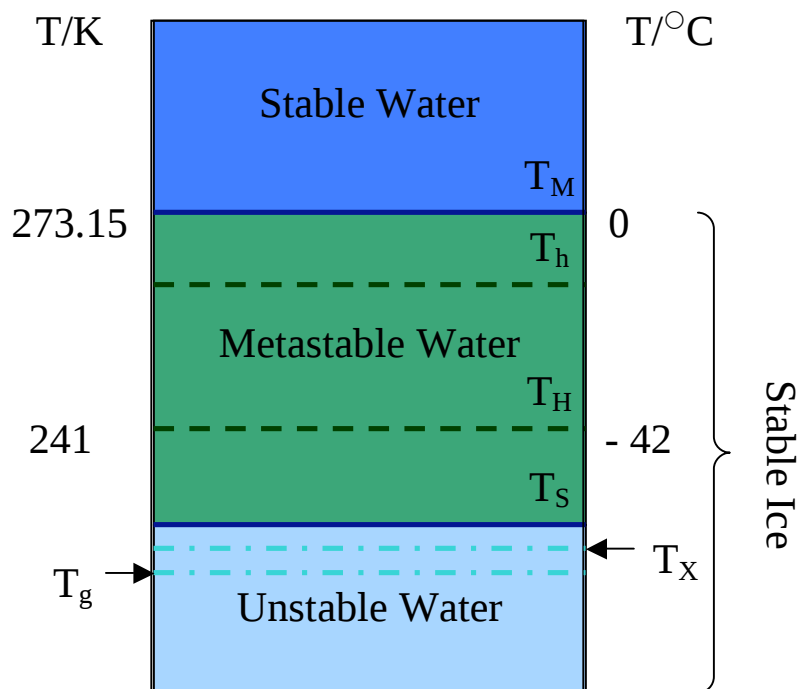


Figure 2. Thermodynamic and kinetic limits for liquid water at atmospheric pressure. The thermodynamic limits for water, the binodal or melting temperature (T_M), and the spinodal or limit of stability (T_S), are system dependent and do not depend on experimental conditions. Although the melting temperature is well known to be 273.15 K, the spinodal is much less well defined as experiments probing the metastable region will first encounter kinetic limits to supercooling. Determining the actual spinodal temperature requires a valid equation of state. Kinetic limits for heterogeneous nucleation (T_h) and homogeneous nucleation ($T_H \approx 231$ K)^{16,17,18} depend on experiment parameters such as sample size, purity, emulsion fluid, etc. Other kinetic limits apply when rapidly cooling liquid water and kinetically arresting its structure. The resulting fluid, glassy water, is defined by the glass transition temperature ($T_g \approx 136$ K)^{21,27,28,29}, and the spontaneous crystallization line T_X .^{21,22}

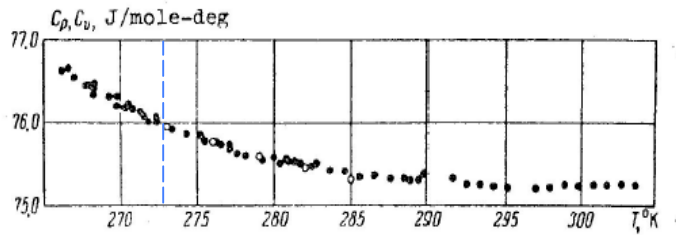


Figure 3. Temperature dependence of the heat capacity of mildly supercooled water at ambient pressure (reproduced from Anisimov, 1972).¹¹ Dashed blue line separates stable and supercooled liquid water regions. Solid circles are the isobaric molar heat capacities C_p at the saturation-vapor pressure; open circles are the isochoric molar heat capacities C_v . In the range 273-285 K the isochoric heat capacities of water have almost the same values as the isobaric heat capacities because the thermal expansion coefficient is close to zero.

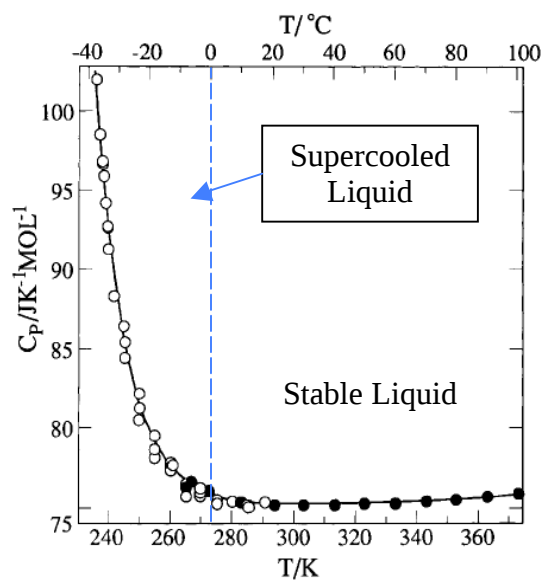


Figure 4. Temperature dependence of the isobaric heat capacity of supercooled ordinary water at ambient pressure (reproduced from Debenedetti, 2003).¹ Solid circles are the measurements of Anisimov *et al.* in 1972.¹¹ Open circles are the 1973 measurements of Angell *et al.*¹²

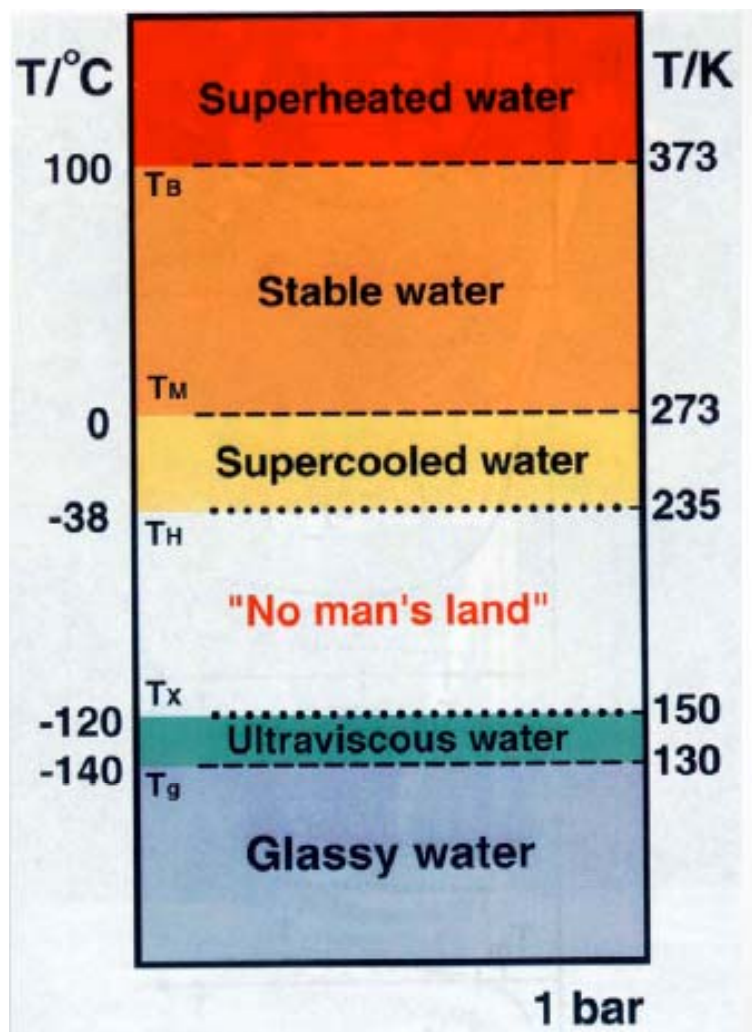


Figure 5. Schematic illustration indicating the various phases of liquid water found at atmospheric pressure, including the region of “No man’s land,” inaccessible to experimentation. Figure courtesy of Dr. O. Mishima.

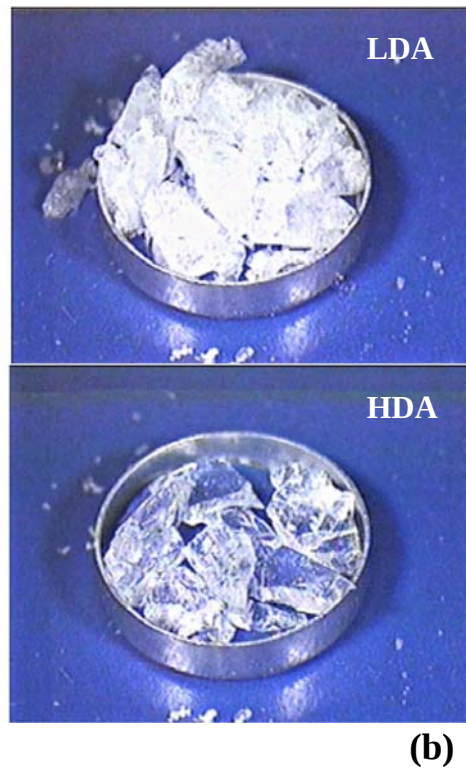
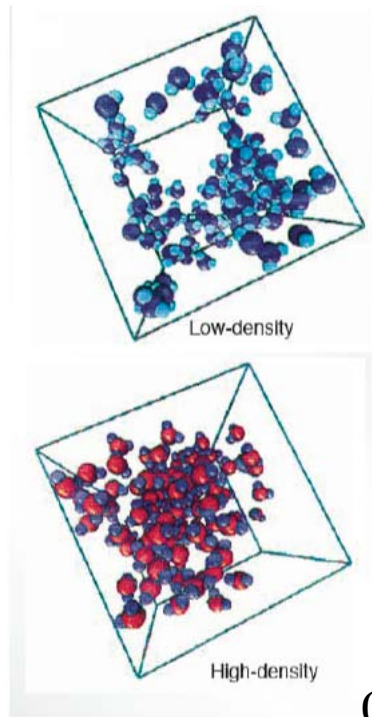


Figure 6. Structure of LDA and HDA. (a) Snapshots of the molecular dynamic configuration of LDA and HDA. (b) Pictures of LDA and HDA samples.
Figures courtesy of O. Mishima.¹¹⁵

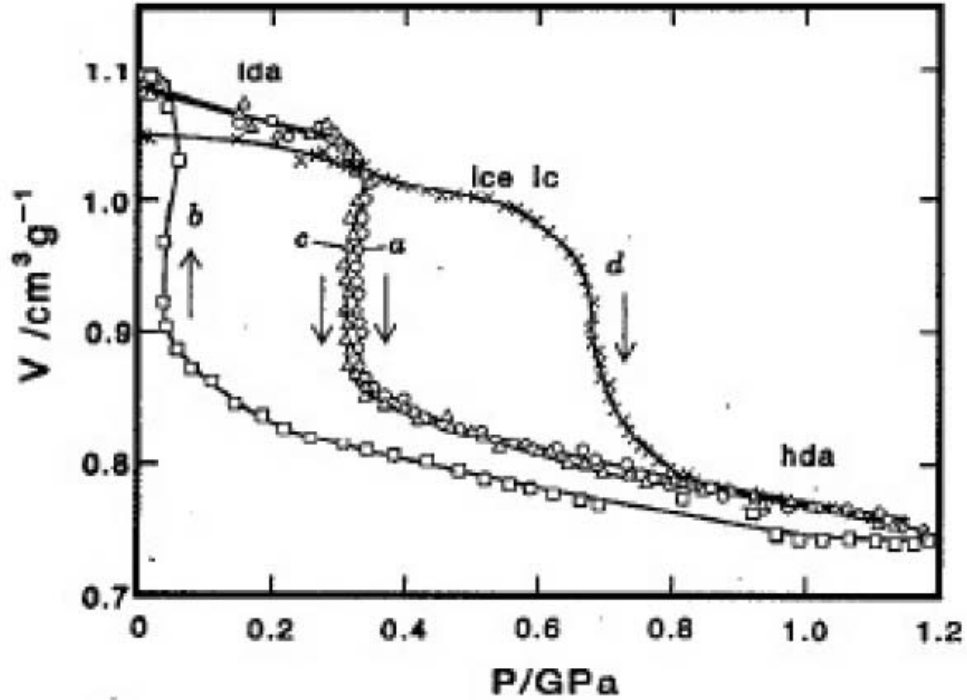


Figure 7. Reversible LDA - HDA phase transition (reproduced from Mishima, 1994).³⁰
The data shows the compression of LDA to HDA (a), the decompression (b) from HDA to LDA and recompression (c) during warming from 130 to 140 K. Curve (d) shows the compression of ice Ic at 145 K.

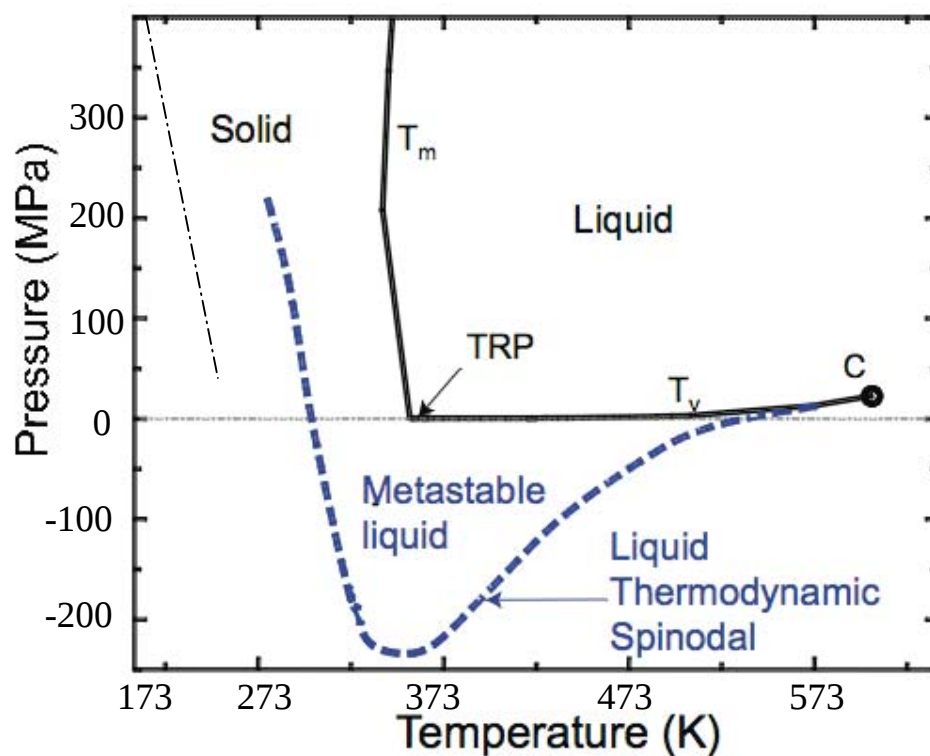


Figure 8. Representation of the stability limit conjecture hypothesis and the retracing liquid spinodal adapted from Figure 2.16, *Metastable Liquids*, P.G. Debenedetti, Princeton, (1996)² and from Angell, (1988).¹¹⁶ Dotted line is 0.1 MPa (1 atm). Dashed line is liquid thermodynamic spinodal. Dash-dotted line is the liquid-solid thermodynamic spinodal. TRP is triple point.

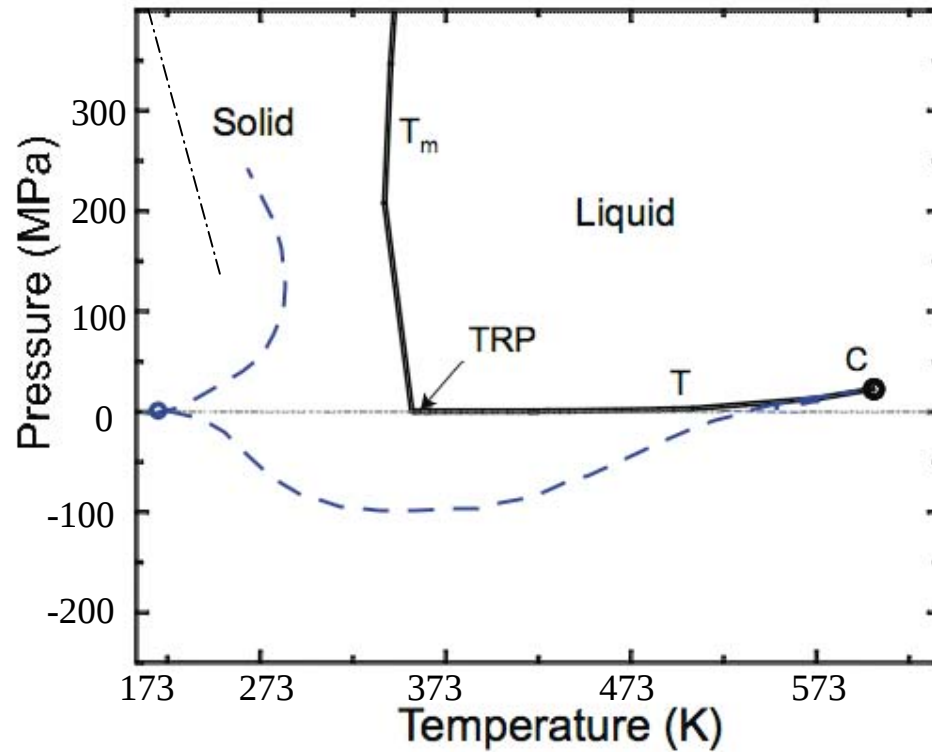


Figure 9. Stability limit conjecture with the thermodynamically consistent lower critical point adapted from Figure 2.16, *Metastable Liquids*, P.G. Debenedetti, Princeton, (1996)² and from Angell, (1988).¹¹⁶ Dotted line is 0.1 MPa (1 atm). Dashed line is liquid thermodynamic spinodal. Dash-dotted line is the liquid-solid thermodynamic spinodal. TRP is triple point.

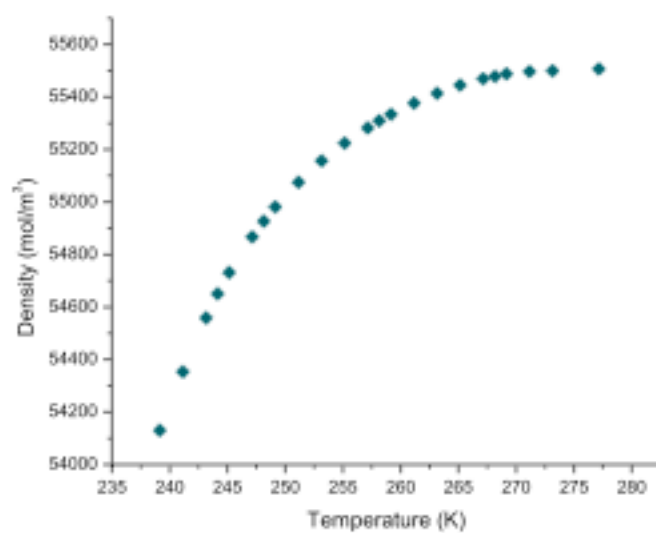


Figure 10. Density of ordinary liquid water at atmospheric pressure (adapted from Zheleznyi, 1969).¹¹⁷

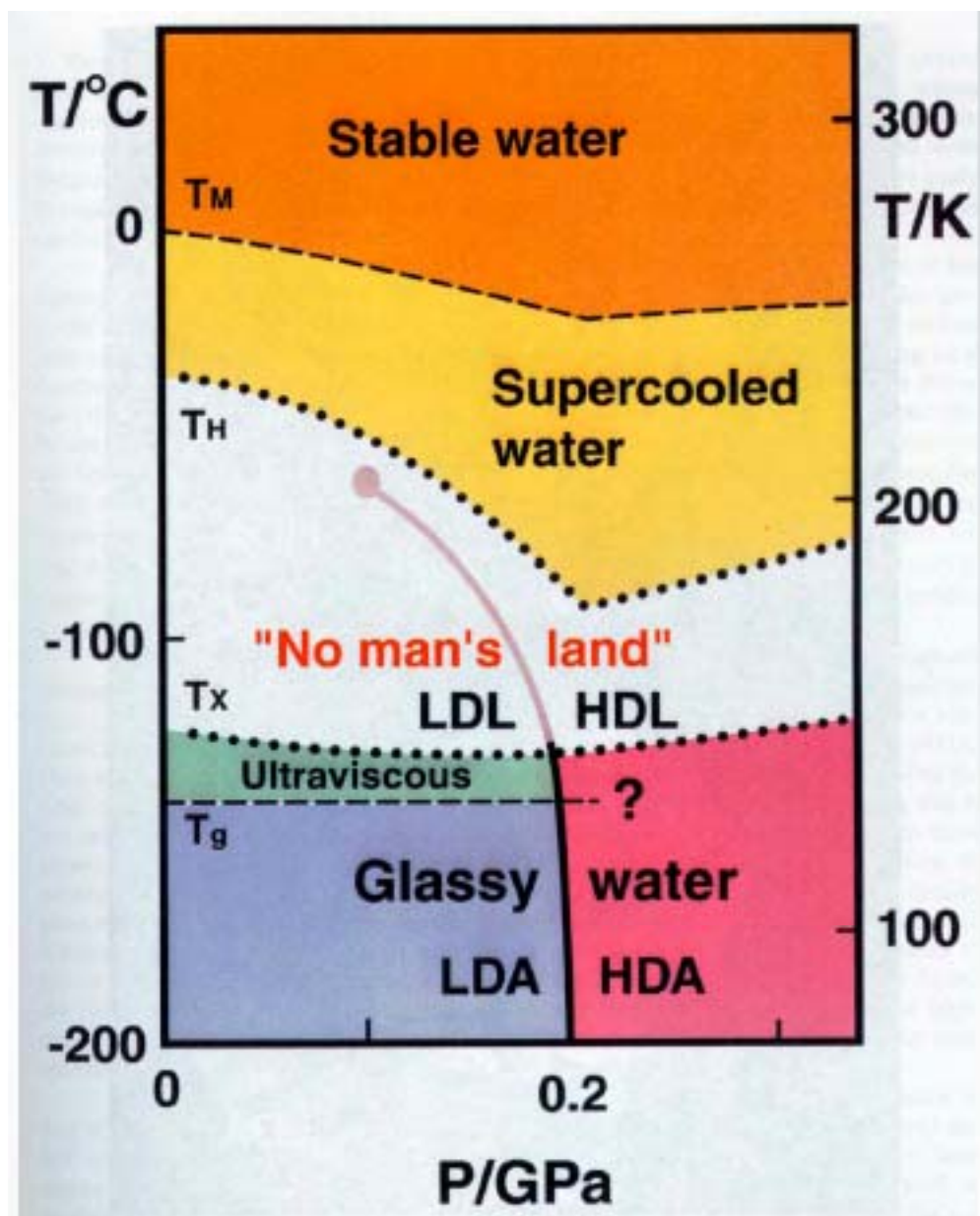


Figure 11. Generalizing Fig. 5 to incorporate pressure and illustrate the second-critical-point scenario. Courtesy of Dr. O. Mishima.

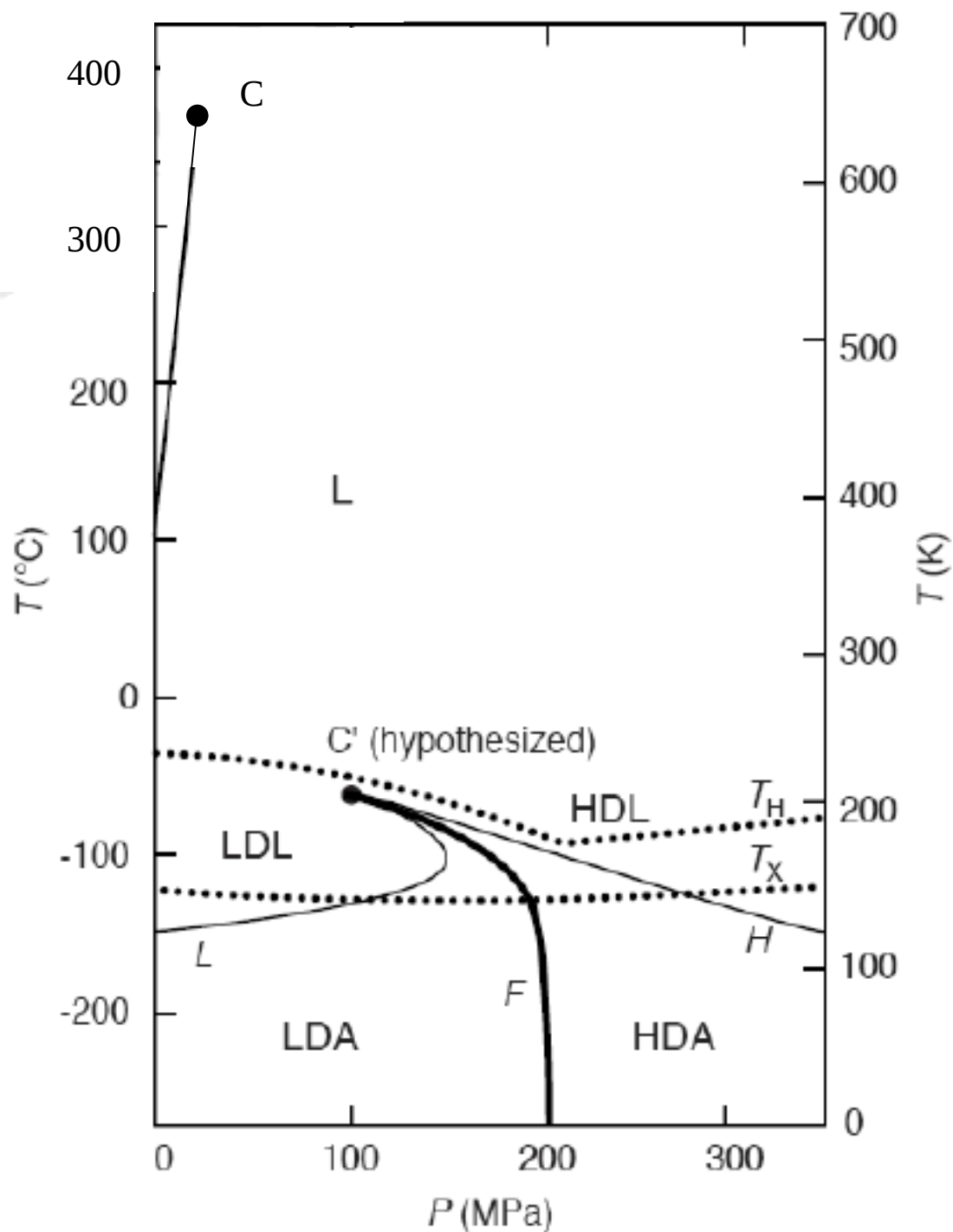


Figure 12. Phase diagram for non-crystalline forms of water, illustrating the second-critical point interpretation (reproduced from Mishima, 1998).⁶¹ C and C' are the vapor-liquid and liquid-liquid critical points respectively. F is the low- and high-density liquid (HDL and LDL) coexistence line and H and L are their limits of stability. At low temperatures, LDL and HDL transition to their respective kinetically arrested amorphous or glassy phases, LDA and HDA.

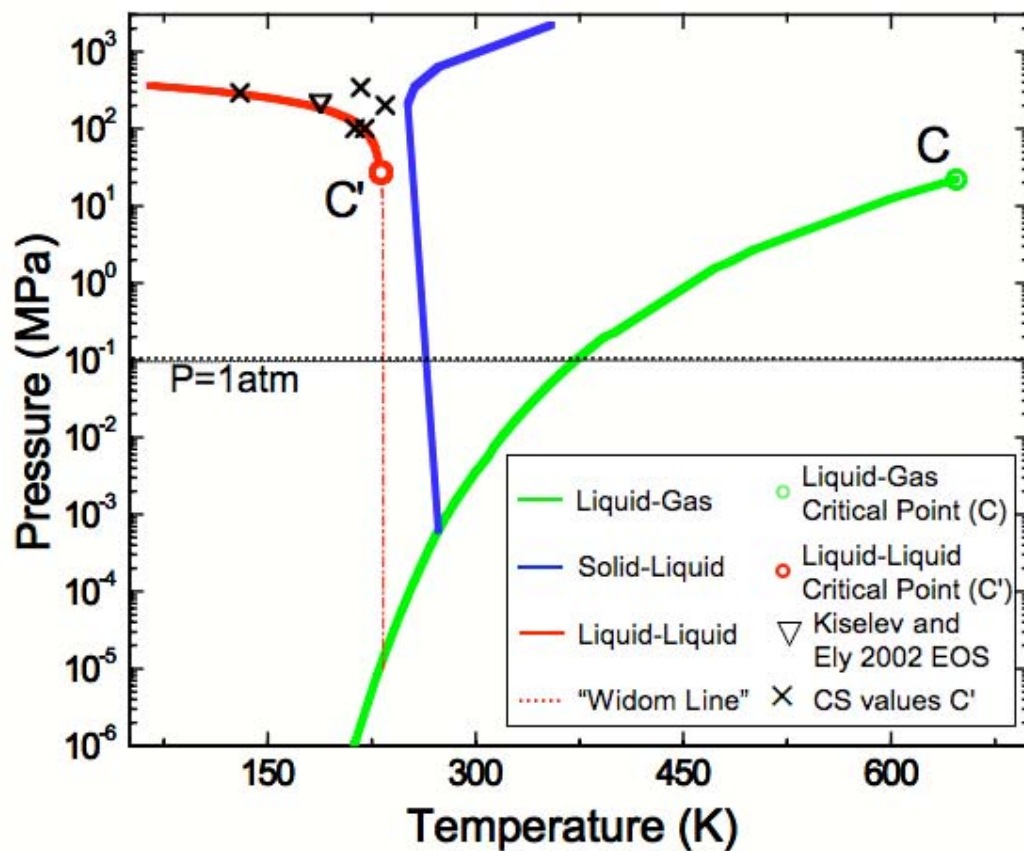


Figure 13. Second-critical-point scenario with computer simulation (CS) values, Kiselev and Ely EOS¹⁰⁸ and our estimate for the second critical point.

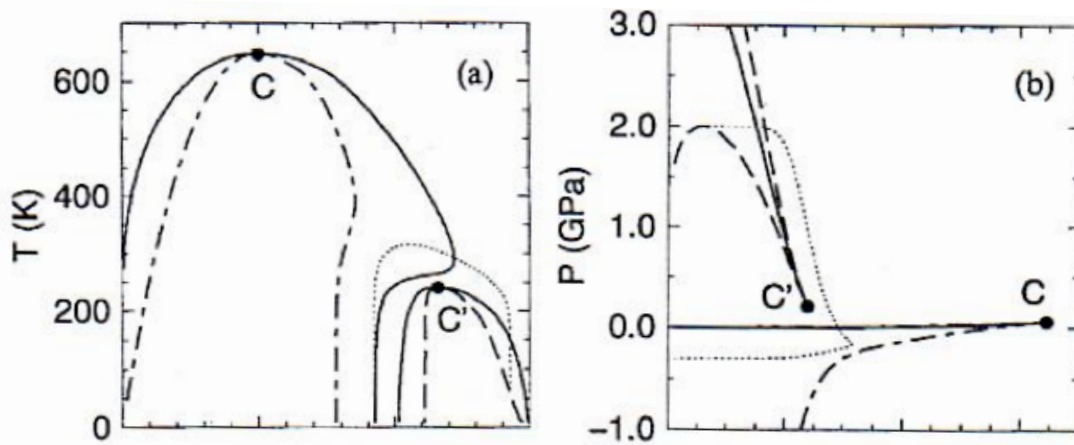


Figure 14. Temperature-density phase diagram illustrating the second-critical-point scenario with spinodal and binodal, generated from an extended van der Waals model (reproduced from Poole *et al.*, 1994).⁶⁰ C and C' are the vapor-liquid and liquid-liquid critical points respectively. The solid curves are coexistence curves, the dashed and dot-dashed lines curves are their corresponding spinodals. The thin dotted line is the TMD locus.

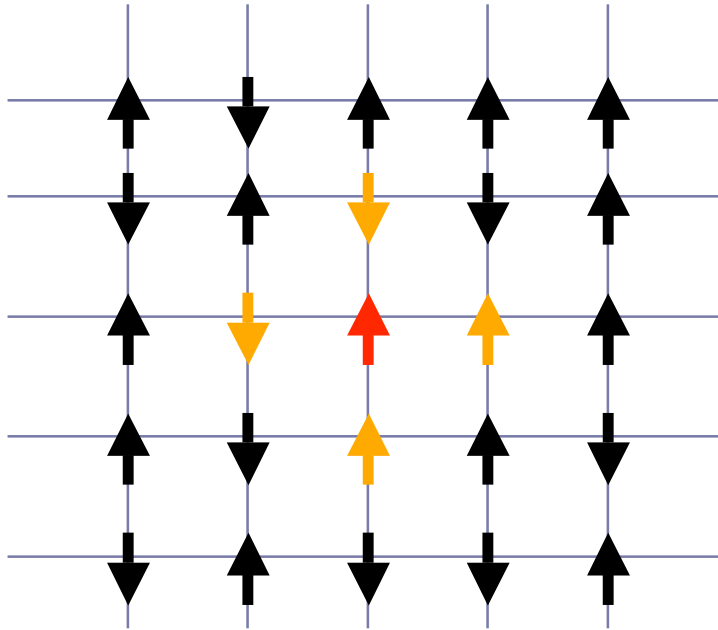


Figure 15. Two dimensional representation of Ising model. The spin direction, or (+) and (-) are influenced by the nearest neighbors, as illustrated by the red vertice and the orange positions that influence it.

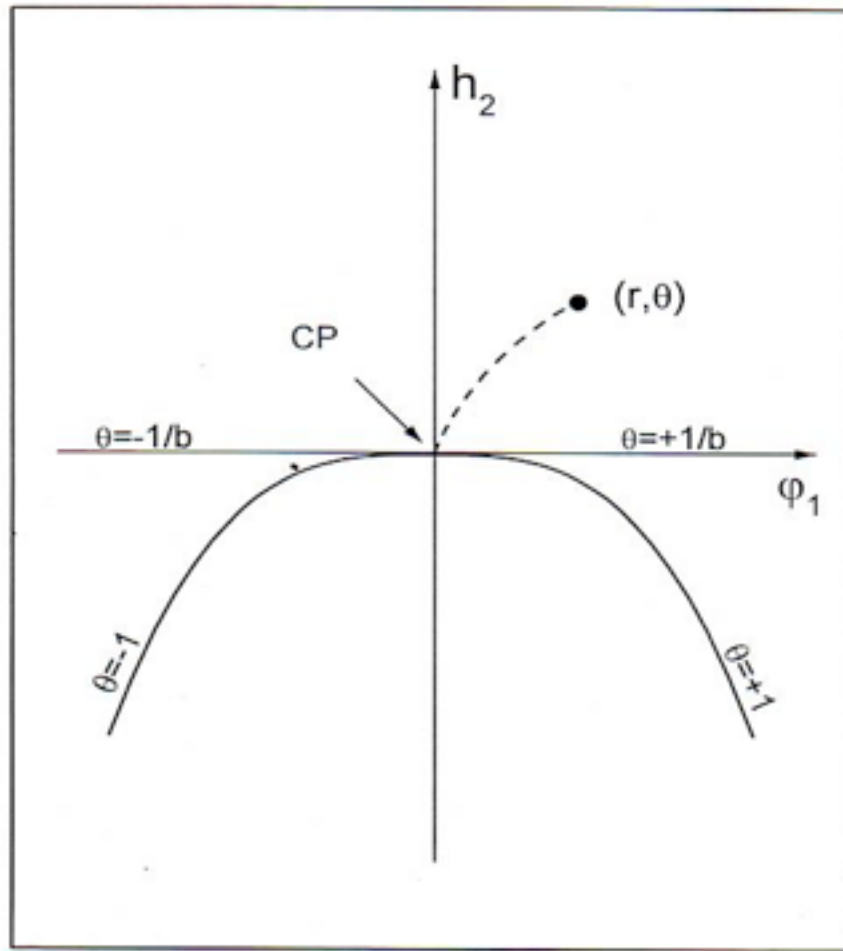


Figure 16. Parametric representation of scaling coordinates $h_1=0$ and $h_2=0$, where r is the distance from the critical point and θ is the angle along a curve of constant r .

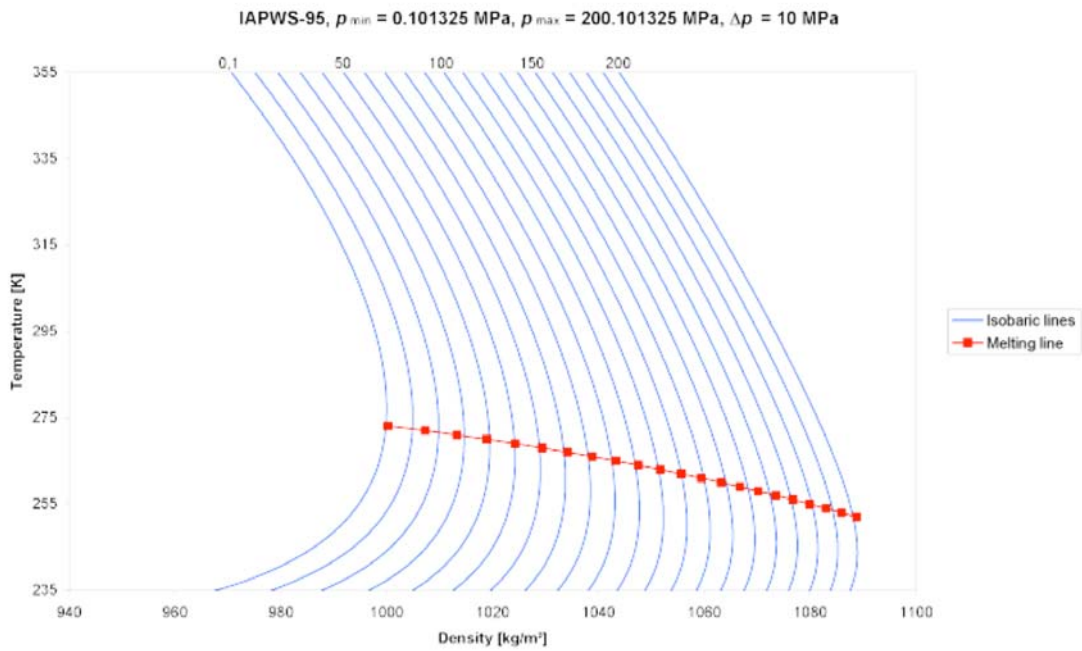


Figure 17. The IAPWS-95 formulation for density at various pressures and temperatures. Figure reproduced from Wagner and Pruß, 2002.³

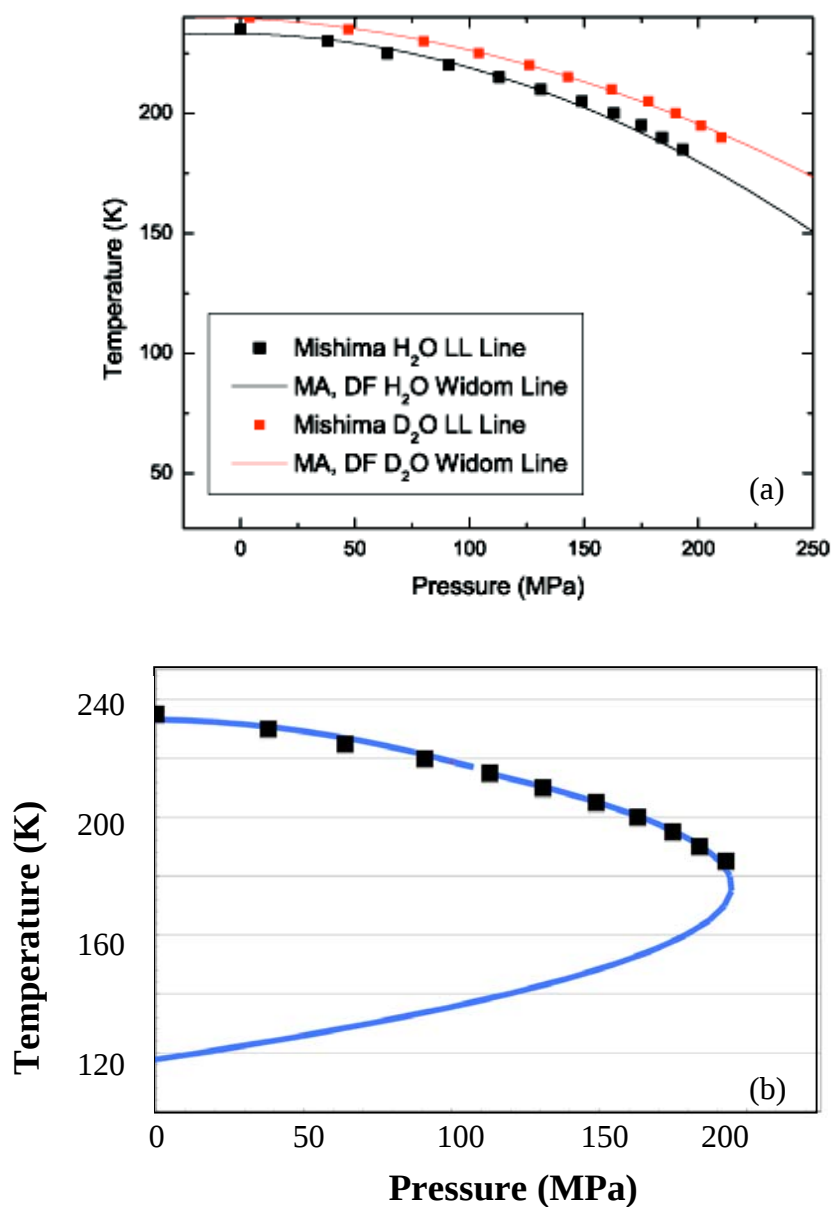


Figure 18. Coexistence curve and “Widom line” for ordinary and heavy water. (a) shows the liquid-liquid coexistence curve courtesy of Mishima⁶² and the fitted curves for the parametric EOS. Figure (b) shows the liquid-liquid coexistence for ordinary water and the predicted curve in the (P,T) plane.

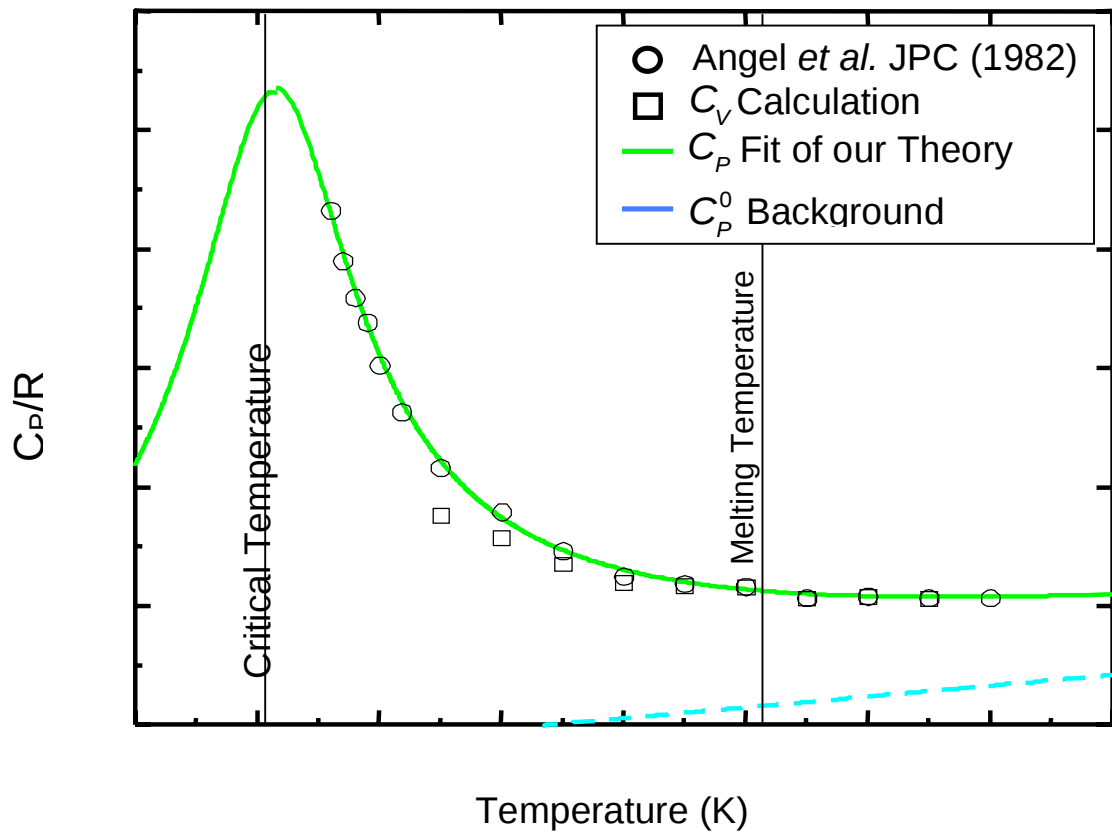


Figure 19. Isobaric heat capacity for ordinary water at atmospheric pressure. Experimental data, from Angell, 1982¹¹⁸ is shown in open circles. Solid green line is the scaled, parametric equation of state, fitted to the data adjusting the location of the critical point $P_C = 27$ MPa, the system-dependent parameter $k/a = 0.45$, and the non-critical background (dashed blue line). Solid vertical lines denote melting temperature and critical temperature.

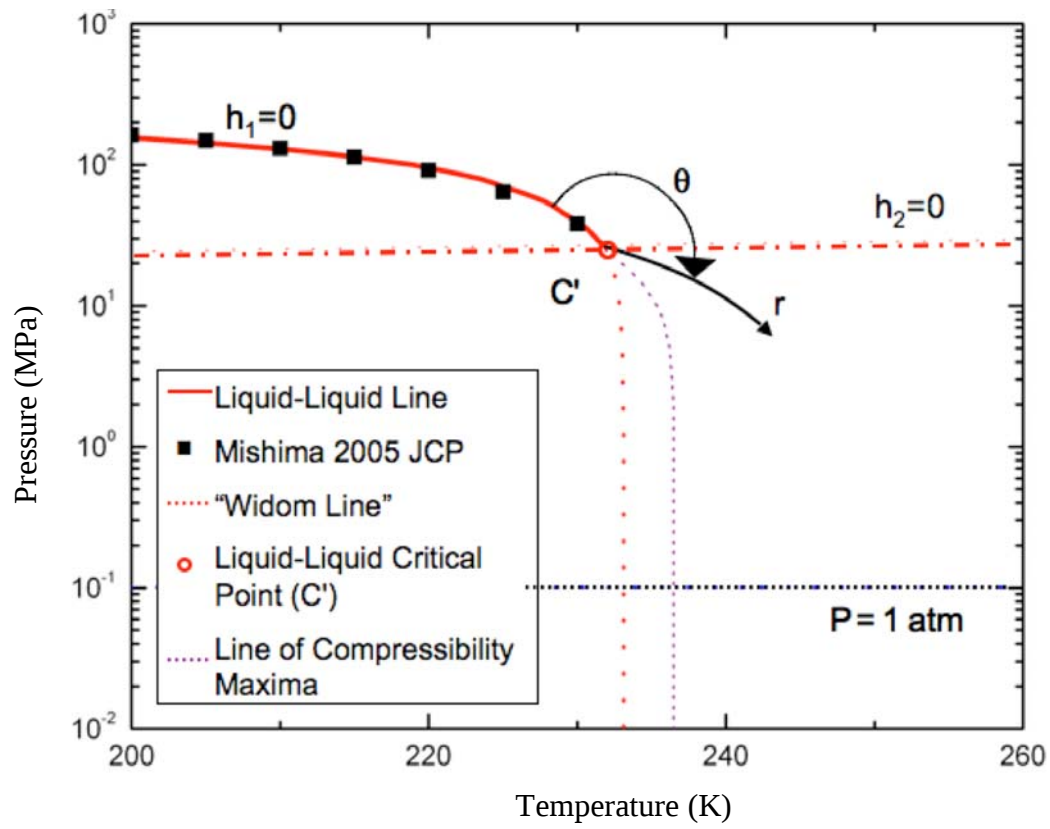


Figure 20. Scaling fields and parametric variables for the scaled parametric equation of state for supercooled liquid water.

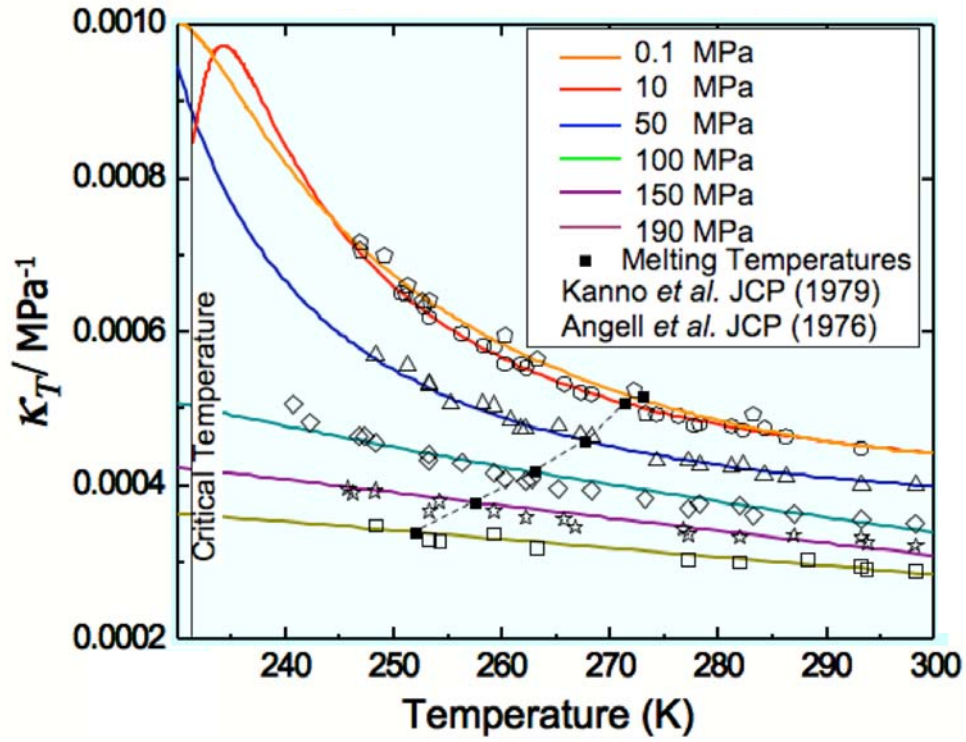


Figure 21. Isothermal compressibility, experimental^{14,15} and predicted for various temperature and pressures. Non-critical background values can be found in Table 4.

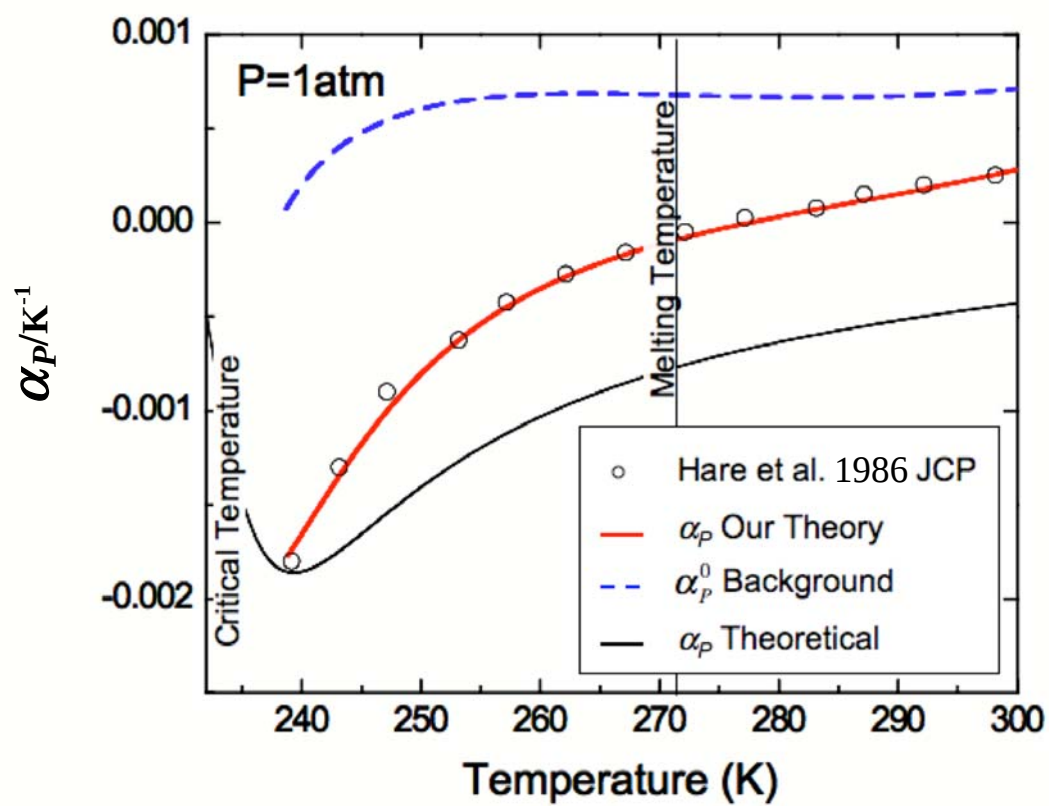


Figure 22. Thermal expansivity at atmospheric pressure, experimental and predicted.¹⁵

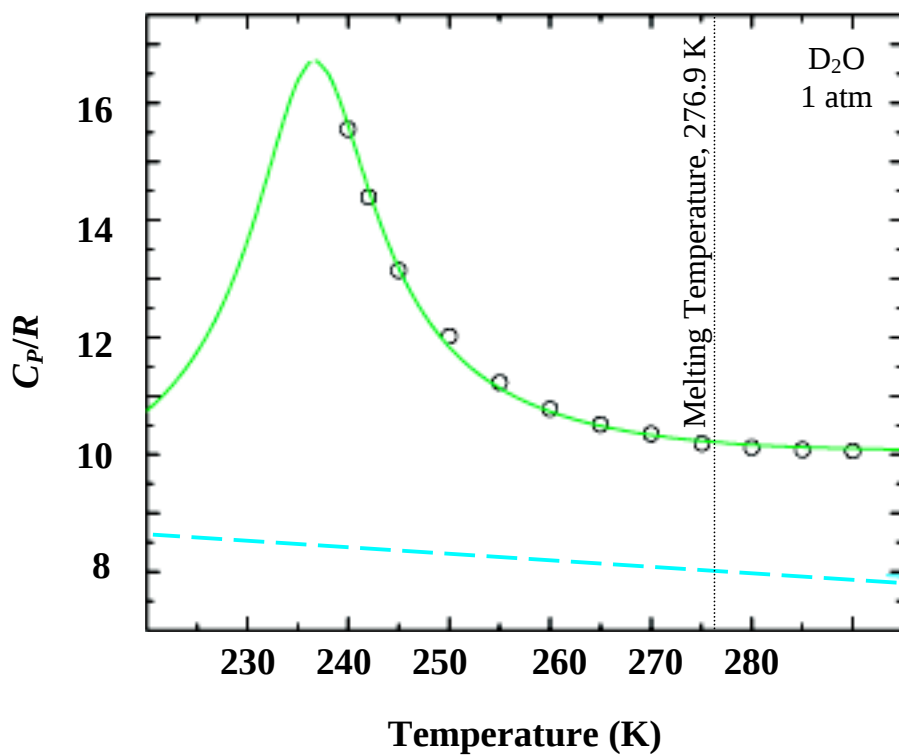


Figure 23. Isobaric heat capacity for heavy water at atmospheric pressure. Experimental data, from Angell, 1982¹¹⁹ is shown in open circles. Solid green line is the scaled, parametric equation of state, fitted to the data adjusting the location of the critical point $P_C = 20$ MPa, the system-dependent parameter $k/a = 0.7$, and the non-critical background (dashed blue line). Dotted vertical line separates stable and metastable liquid water.

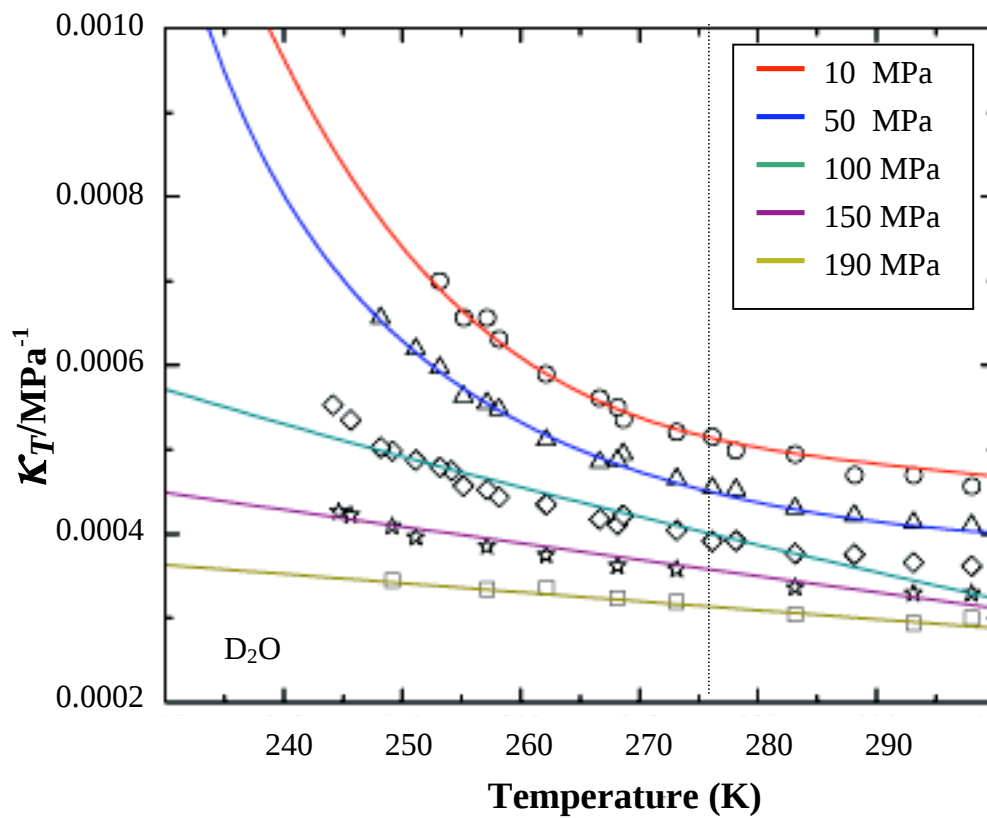


Figure 24. Isothermal compressibility for heavy water at various temperatures and pressures. Experimental data, from Kanno *et al.*, 1982¹⁴ is shown in open data points. Solid lines are predicted from the equation of state. Non-critical background values can be found in Table 4. Vertical dotted line is the melting temperature for heavy water.

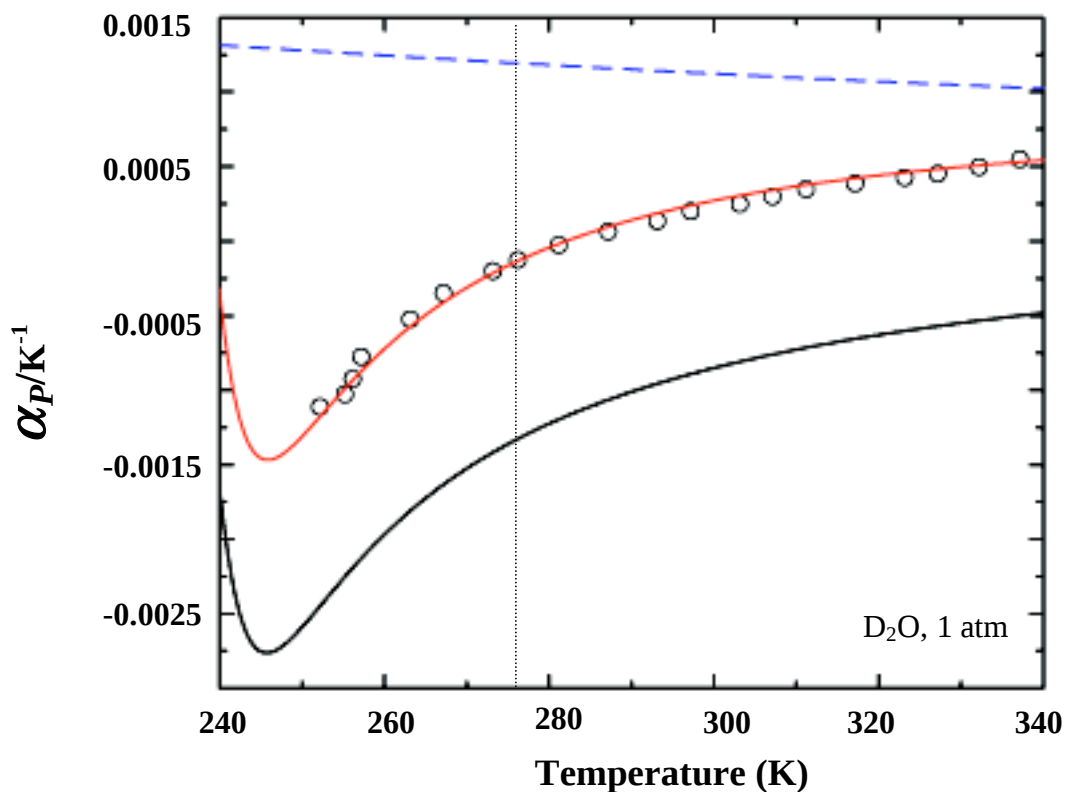


Figure 25. Thermal expansivity for heavy water at atmospheric pressure. Experimental data, from Hare *et al.*, 1986¹⁵ is shown in open circles. Solid lines, α_p without non-critical background in black and α_p with background in red, are predicted from the equation of state. Non-critical background values can be found in Table 4. Vertical dotted line is the melting temperature for heavy water.

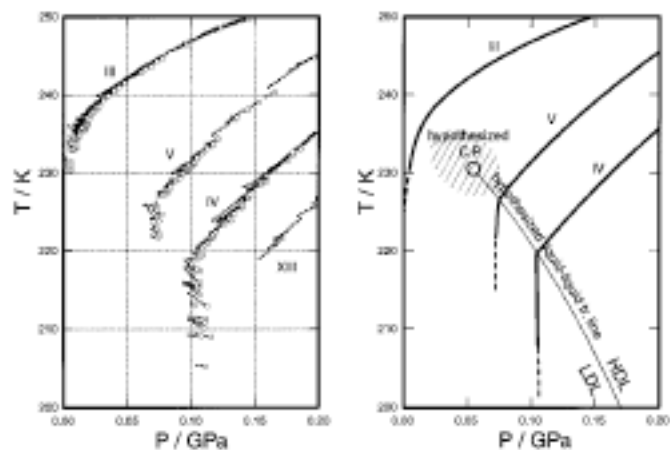


Figure 26. Melting curves of D₂O ices (III, V, IV, XIII) (reproduced from Mishima, 2000).⁶³ (a) Experimental results (b) Schematic showing hypothesized liquid-liquid transition between high-and low-density liquid (HDL, LDL). C.P. denotes the hypothesized critical point.

APPENDIX III: DERIVATIONS

I. Calculating mixing coefficients from liquid-liquid coexistence curve and the “Widom line”

$$h_1 = \frac{a_1 \Delta P}{\rho_c R T_c} + \frac{a_2 \Delta T}{T_c} + \frac{a_3 \Delta P^2}{(\rho_c R T_c)^2}$$

$$h_2 = \frac{b_1 \Delta T}{T_c} + \frac{b_2 \Delta P}{\rho_c R T_c}$$

where $\Delta P = P - P_c$ and $\Delta T = T - T_c$

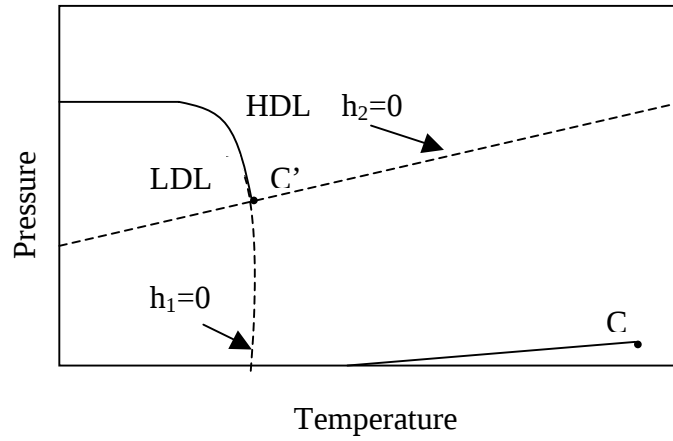


Figure 1. Phase Diagram for non-crystalline forms of water showing second-critical point interpretation. C and C' are vapour-liquid and liquid-liquid critical points, respectively. C', the critical point for high and low density liquid water (HDL and LDL) occurs at 100MPa and 220K.

The dashed perpendicular lines in the phase diagram above represent the case of $h_1 = 0$ and $h_2 = 0$. The almost vertical axis of $h_1 = 0$ corresponds with the phase transition between HDL and LDL supercooled liquid water.

$$\left(\frac{\Delta P}{\Delta T} \right)_{h_1=0} = -\frac{a_2}{a_1}, \quad \left(\frac{\Delta P}{\Delta T} \right)_{h_2=0} = -\frac{b_1}{b_2}$$

Data points representing a best guess for the homogeneous nucleation limit, believed by O. Mishima to be very close to the liquid-liquid coexistence curve ($h_1=0$), were originally obtained from Mishima *et al.*¹ and then through personal communications between M.A.

¹ O. Mishima and H.E. Stanley, Nature **396**, 329 (1998).

Anisimov and O. Mishima in 2005 and 2007. The points were fitted with a parabolic polynomial, see Fig. 2, to obtain an equation for the “Widom line.” The fit with O. Mishima’s data for the liquid-liquid coexistence curve in ordinary water produced the result of:

$$T = A + BP + CP^2 = 234.12983428512246 - 0.06175940215384P - 0.000952783743374272P^2$$

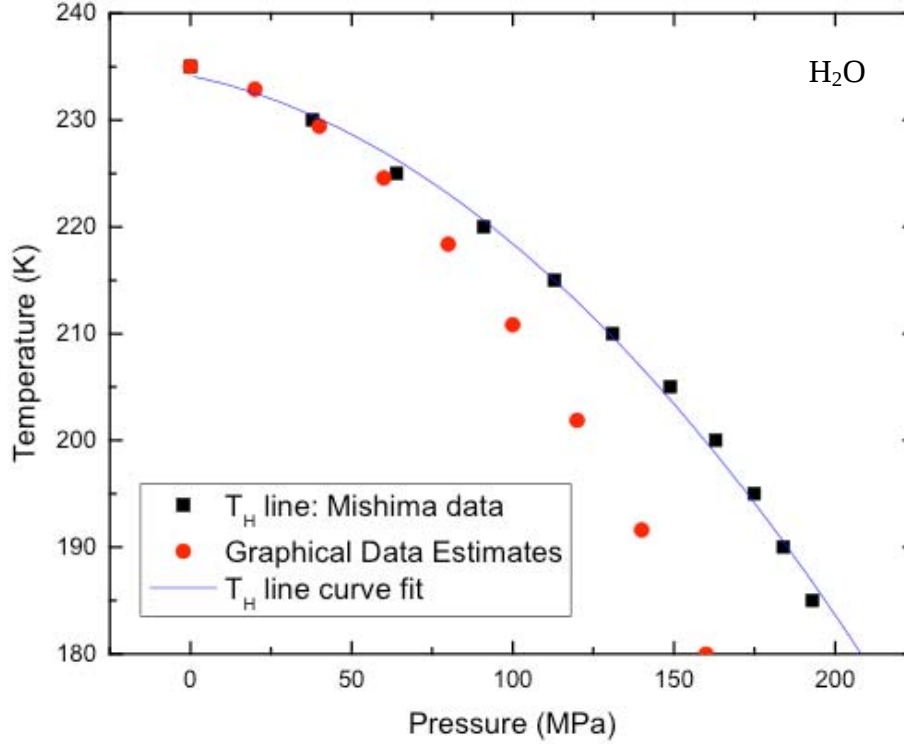


Figure 2. Estimation for the homogeneous nucleation temperature, T_H , at various pressures in supercooled liquid water. Red circles represent data points extrapolated from a figure in the 1998 Nature publication of Mishima *et al.*¹ The sensitivity of the equation of state to the location of the coexistence curve and its extension beyond the critical point, the “Widom line”, resulted in further communication with O. Mishima. The black squares represent a more accurate estimate of T_H at various pressures, provided by O. Mishima through personal communication with M.A. Anisimov.

Adjusting the equation to fit $h_1 = 0 = a_1\Delta\tilde{P} + a_2\Delta\tilde{T} + a_3\Delta\tilde{P}^2$:

$$(T - T_c) + T_c = A + B(P - P_c) + BP_c + C(P - P_c)^2 + 2CPP_c - CP_c^2$$

where

$$A = 233.129834,$$

$$B = -0.0167594,$$

$$C = -0.0012528$$

$$\Delta T = [A - T_c + BP_c - CP_c^2 + 2CP_c^2] + [B + 2CP_c]\Delta P + C\Delta P^2$$

Rearranging, we find:

$$0 = [A - T_c + BP_c - CP_c^2 + 2CP_c^2] + [B + 2CP_c]\Delta P - \Delta T + C\Delta P^2$$

The variables can be made dimensionless by dividing the equation by $(\rho_c RT_c)^2$.

Multiplying by $-\rho_c^2 R^2 T_c$ gives our ΔT term a coefficient of 1.

$$0 = -\frac{[A - T_c + BP_c - CP_c^2 + 2CP_c^2]}{T_c} - \rho_c R [B + 2CP_c] \Delta \tilde{P} + \Delta \tilde{T} - \rho_c^2 R^2 T_c C \Delta \tilde{P}^2$$

Comparing to $h_1 = 0 = a_1 \Delta \tilde{P} + a_2 \Delta \tilde{T} + a_3 \Delta \tilde{P}^2$ and collecting terms with like powers of pressure and temperature yields values for the coefficients:

$$0 = -\frac{A - T_c + BP_c - CP_c^2 + 2CP_c^2}{T_c} \checkmark$$

$$a_1 = -\rho_c R [2CP_c + B]$$

$$a_2 = 1$$

$$a_3 = -\rho_c^2 R^2 T_c C$$

We obtain values for our coefficients by using literature estimates of the critical pressure. The actual position of the critical point along the ‘Widom line’ will be estimated later through trial and error comparisons between experimental data and calculated values for heat capacity.

$$\text{Using } R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}, P_c = 100 \text{ MPa, and } \rho_c = \frac{1 \text{ g cm}^{-3}}{18 \text{ g mol}^{-1}} \frac{100^3 \text{ cm}^3}{\text{m}^3} = 55555.6 \text{ mol m}^{-3},$$

we find $T_c = 218 \text{ K}$,

and our equation

$$h_1 = a_1 \Delta \tilde{P} + a_2 \Delta \tilde{T} + a_3 \Delta \tilde{P}^2$$

Where $a_1 = 0.039$, $a_2 = 1$, and $a_3 = 0.062$.

This analysis also shows $b_1 = 0.039$ and $b_2 = -1$, given that the respective slopes are perpendicular to each other,

$$-\frac{a_2}{a_1} = -\frac{1}{-b_1 / b_2} = \frac{b_2}{b_1}.$$

A similar calculation for heavy water was performed. O. Mishima provided a best guess for the location of the liquid-liquid line. A polynomial fit for the data resulted in:

$$\begin{aligned} A &= 239.62382, \\ B &= -0.045217, \\ C &= -0.0008772 \end{aligned}$$

Solving the algebra results in mixing coefficients of

$$h_1 = a_1 \Delta \tilde{P} + a_2 \Delta \tilde{T} + a_3 \Delta \tilde{P}^2$$

Where $a_1 = 0.042$, $a_2 = 1$, and $a_3 = 0.042$.

II. Derivations for Thermodynamic Properties based on Universal Equations and Theoretical Variables

$$h_1 = a_1 \Delta \tilde{P} + a_2 \Delta \tilde{T} + a_3 \Delta \tilde{P}^2$$

$$h_2 = b_1 \Delta \tilde{T} + b_2 \Delta \tilde{P}$$

where $\Delta \tilde{P} = (P - P_c) / (\rho_c R T_c)$ and $\Delta \tilde{T} = (T - T_c) / T_c$

Inverting the equations for h_1 and h_2 , we can express ΔT and ΔP in terms of h_1 and h_2 .

$$\Delta \tilde{T} = \frac{a_1}{a_1 b_1 - a_2 b_2} h_2 - \frac{b_2}{a_1 b_1 - a_2 b_2} h_1^{**}$$

$$\Delta \tilde{P} = \frac{b_1}{a_1 b_1 - a_2 b_2} h_1 - \frac{a_2}{a_1 b_1 - a_2 b_2} h_2^{**}$$

** Only if discounting a_3 and b_3 or defining the first term to include the third term.

The field-dependent dimensionless density of a relevant thermodynamic potential relates to scaling “densities” conjugate to h_1 and h_2 , and strongly and weakly divergent susceptibilities associated with the densities.

$$\Delta \tilde{G}(h_1, h_2) = \frac{\Delta G}{V \rho_c R T_c}$$

$$\varphi_1 = -\left(\frac{\partial \Delta \tilde{G}}{\partial h_1}\right)_{h_2}, \quad \varphi_2 = -\left(\frac{\partial \Delta \tilde{G}}{\partial h_2}\right)_{h_1}, \quad \chi_1 = \left(\frac{\partial \varphi_1}{\partial h_1}\right)_{h_2}, \quad \chi_2 = \left(\frac{\partial \varphi_2}{\partial h_2}\right)_{h_1},$$

$$\chi_{12} = \chi_{21} = \left(\frac{\partial \varphi_1}{\partial h_2}\right)_{h_1} = \left(\frac{\partial \varphi_2}{\partial h_1}\right)_{h_2}$$

Using Jacobians to change variables:

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{\partial(S,V)}{\partial(T,V)} = \frac{\partial(S,V)/\partial(T,P)}{\partial(T,V)/\partial(T,P)} = \frac{\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T - \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial T}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T - \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_T}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{\left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial V}{\partial P}\right)_T - \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial S}{\partial P}\right)_T}{\left(\frac{\partial V}{\partial P}\right)_T}$$

$$\varphi_1 = -\left(\frac{\partial \Delta \tilde{G}}{\partial h_1}\right)_{h_2} = -\frac{\partial(\Delta \tilde{G}, h_2)/\partial(\Delta \tilde{T}, \Delta \tilde{P})}{\partial(h_1, h_2)/\partial(\Delta \tilde{T}, \Delta \tilde{P})}$$

$$= -\frac{\left(\frac{\partial \Delta \tilde{G}}{\partial \Delta \tilde{T}}\right)_{\Delta \tilde{P}} \left(\frac{\partial h_2}{\partial \Delta \tilde{P}}\right)_{\Delta \tilde{T}} - \left(\frac{\partial h_2}{\partial \Delta \tilde{T}}\right)_{\Delta \tilde{P}} \left(\frac{\partial \Delta \tilde{G}}{\partial \Delta \tilde{P}}\right)_{\Delta \tilde{T}}}{\left(\frac{\partial h_1}{\partial \Delta \tilde{T}}\right)_{\Delta \tilde{P}} \left(\frac{\partial h_2}{\partial \Delta \tilde{P}}\right)_{\Delta \tilde{T}} - \left(\frac{\partial h_2}{\partial \Delta \tilde{T}}\right)_{\Delta \tilde{P}} \left(\frac{\partial h_1}{\partial \Delta \tilde{P}}\right)_{\Delta \tilde{T}}}$$

$$\varphi_2 = -\left(\frac{\partial \Delta \tilde{G}}{\partial h_2}\right)_{h_1} = -\frac{\partial(\Delta \tilde{G}, h_1)/\partial(\Delta \tilde{T}, \Delta \tilde{P})}{\partial(h_2, h_1)/\partial(\Delta \tilde{T}, \Delta \tilde{P})}$$

$$= -\frac{\left(\frac{\partial \Delta \tilde{G}}{\partial \Delta \tilde{T}}\right)_{\Delta \tilde{P}} \left(\frac{\partial h_1}{\partial \Delta \tilde{P}}\right)_{\Delta \tilde{T}} - \left(\frac{\partial h_1}{\partial \Delta \tilde{T}}\right)_{\Delta \tilde{P}} \left(\frac{\partial \Delta \tilde{G}}{\partial \Delta \tilde{P}}\right)_{\Delta \tilde{T}}}{\left(\frac{\partial h_2}{\partial \Delta \tilde{T}}\right)_{\Delta \tilde{P}} \left(\frac{\partial h_1}{\partial \Delta \tilde{P}}\right)_{\Delta \tilde{T}} - \left(\frac{\partial h_1}{\partial \Delta \tilde{T}}\right)_{\Delta \tilde{P}} \left(\frac{\partial h_2}{\partial \Delta \tilde{P}}\right)_{\Delta \tilde{T}}}$$

$$a_{1eff} = a_1 + 2a_3\Delta P, \quad b_{1eff} = b_1 + 2b_3\Delta T$$

$$\left(\frac{\partial h_1}{\partial \Delta \tilde{P}} \right)_{\Delta T} = a_{1eff}, \quad \left(\frac{\partial h_1}{\partial \Delta \tilde{T}} \right)_{\Delta P} = a_2,$$

$$\left(\frac{\partial h_2}{\partial \Delta \tilde{T}} \right)_{\Delta P} = b_{1eff}, \quad \left(\frac{\partial h_2}{\partial \Delta \tilde{P}} \right)_{\Delta T} = b_2$$

Using Jacobians,

$$\left(\frac{\partial \Delta \tilde{P}}{\partial h_1} \right)_{h_2} = \frac{b_{1eff}}{a_{1eff}b_{1eff} - a_2b_2}, \quad \left(\frac{\partial \Delta \tilde{P}}{\partial h_2} \right)_{h_1} = -\frac{a_2}{a_{1eff}b_{1eff} - a_2b_2}$$

$$\left(\frac{\partial \Delta \tilde{T}}{\partial h_1} \right)_{h_2} = -\frac{b_2}{a_{1eff}b_{1eff} - a_2b_2}, \quad \left(\frac{\partial \Delta \tilde{T}}{\partial h_2} \right)_{h_1} = \frac{a_{1eff}}{a_{1eff}b_{1eff} - a_2b_2}$$

$$\frac{1}{R} \left(\frac{\partial \Delta G}{\partial T} \right)_P = -\Delta \tilde{S}, \text{ from } dG = VdP - SdT$$

$$\frac{P_c}{RT_c} \left(\frac{\partial \Delta G}{\partial P} \right)_T = \Delta \tilde{V}, \text{ from } dG = VdP - SdT$$

$$\varphi_1 = - \left[\frac{-b_2\Delta \tilde{S} - b_{1eff}\Delta \tilde{V}}{a_2b_2 - a_{1eff}b_{1eff}} \right] = \left[\frac{-b_{1eff}\Delta \tilde{V} - b_2\Delta \tilde{S}}{a_{1eff}b_{1eff} - a_2b_2} \right]$$

$$\varphi_2 = - \left[\frac{-a_{1eff}\Delta \tilde{S} - a_2\Delta \tilde{V}}{a_{1eff}b_{1eff} - a_2b_2} \right] = \left[\frac{a_{1eff}\Delta \tilde{S} + a_2\Delta \tilde{V}}{a_{1eff}b_{1eff} - a_2b_2} \right]$$

These densities conjugate to the scaling fields are linear combinations of the physical densities $\Delta V = V - V_c$ and $\Delta S = S - S_c$.

Rearranging, we can solve for ΔV and ΔS in terms of φ_1 and φ_2 .

$$\Delta \tilde{V} = \frac{\varphi_1(a_{1eff}b_{1eff} - a_2b_2) + b_2\Delta \tilde{S}}{-b_{1eff}}, \quad \Delta \tilde{S} = \frac{\varphi_1(a_{1eff}b_{1eff} - a_2b_2) + b_{1eff}\Delta \tilde{V}}{-b_2}$$

$$\Delta \tilde{V} = \frac{\varphi_2(a_{1eff}b_{1eff} - a_2b_2) - a_{1eff}\Delta \tilde{S}}{a_2}, \quad \Delta \tilde{S} = \frac{\varphi_2(a_{1eff}b_{1eff} - a_2b_2) - a_2\Delta \tilde{V}}{a_{1eff}}$$

$$\Delta \tilde{V} = \left(\frac{\partial \Delta \tilde{G}}{\partial \Delta \tilde{P}} \right)_{\Delta \tilde{T}} = - \left(a_{1eff} \varphi_1 + b_2 \varphi_2 \right)$$

$$\Delta \tilde{S} = - \left(\frac{\partial \Delta \tilde{G}}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} = \left(a_2 \varphi_1 + b_{1eff} \varphi_2 \right)$$

using Maxwell Relations, $\left(\frac{\partial S}{\partial P} \right)_T = -V \left(\frac{\partial V}{\partial T} \right)_P$, and $\left(\frac{\partial S}{\partial T} \right)_P = \frac{Cp}{T}$

$$\left(\frac{\partial \Delta \tilde{S}}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} = \left(a_2 \left(\frac{\partial \varphi_1}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} + b_1 \left(\frac{\partial \varphi_2}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} \right)$$

$$\left(\frac{\partial \varphi_1}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} = \frac{\partial \left(\varphi_1, \Delta \tilde{P} \right) / \partial (h_1, h_2)}{\partial \left(\Delta \tilde{T}, \Delta \tilde{P} \right) / \partial (h_1, h_2)} = \frac{\left(\frac{\partial \varphi_1}{\partial h_1} \right)_{h_2} \left(\frac{\partial \Delta \tilde{P}}{\partial h_2} \right)_{h_1} - \left(\frac{\partial \Delta \tilde{P}}{\partial h_1} \right)_{h_2} \left(\frac{\partial \varphi_1}{\partial h_2} \right)_{h_1}}{\left(\frac{\partial \Delta \tilde{T}}{\partial h_1} \right)_{h_2} \left(\frac{\partial \Delta \tilde{P}}{\partial h_2} \right)_{h_1} - \left(\frac{\partial \Delta \tilde{P}}{\partial h_1} \right)_{h_2} \left(\frac{\partial \Delta \tilde{T}}{\partial h_2} \right)_{h_1}}$$

$$\left(\frac{\partial \varphi_1}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} = \left(a_2 \chi_1 + b_{1eff} \chi_{12} \right)$$

$$\left(\frac{\partial \varphi_2}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} = \frac{\partial \left(\varphi_2, \Delta \tilde{P} \right) / \partial (h_1, h_2)}{\partial \left(\Delta \tilde{T}, \Delta \tilde{P} \right) / \partial (h_1, h_2)} = \frac{\left(\frac{\partial \varphi_2}{\partial h_1} \right)_{h_2} \left(\frac{\partial \Delta \tilde{P}}{\partial h_2} \right)_{h_1} - \left(\frac{\partial \Delta \tilde{P}}{\partial h_1} \right)_{h_2} \left(\frac{\partial \varphi_2}{\partial h_2} \right)_{h_1}}{\left(\frac{\partial \Delta \tilde{T}}{\partial h_1} \right)_{h_2} \left(\frac{\partial \Delta \tilde{P}}{\partial h_2} \right)_{h_1} - \left(\frac{\partial \Delta \tilde{P}}{\partial h_1} \right)_{h_2} \left(\frac{\partial \Delta \tilde{T}}{\partial h_2} \right)_{h_1}}$$

$$\left(\frac{\partial \varphi_2}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} = a_2 \chi_{12} + b_{1eff} \chi_2$$

and

$$\left(\frac{\partial \Delta \tilde{S}}{\partial \Delta T} \right)_{\Delta P} = \left(a_2^2 \chi_1 + 2a_2 b_{1eff} \chi_{12} + b_{1eff}^2 \chi_2 \right) = \frac{C_p - C_p^r}{T}$$

The universal form of the heat capacity is:

$$C_p = T \left(a_2^2 \chi_1 + 2a_2 b_{1eff} \chi_{12} + b_{1eff}^2 \chi_2 \right) + C_p^r$$

where r designates the residual, or background, heat capacity.

Heat capacity at constant volume can also be calculated.

$$\frac{C_v}{T} = \left(\frac{\partial S}{\partial T} \right)_v = \frac{\partial(S, V) / \partial(T, P)}{\partial(T, V) / \partial(T, P)} = \frac{\left(\frac{\partial S}{\partial T} \right)_p \left(\frac{\partial V}{\partial P} \right)_T - \left(\frac{\partial S}{\partial P} \right)_T \left(\frac{\partial V}{\partial T} \right)_p}{\left(\frac{\partial T}{\partial T} \right)_p \left(\frac{\partial V}{\partial P} \right)_T - \left(\frac{\partial T}{\partial P} \right)_T \left(\frac{\partial V}{\partial T} \right)_p} =$$

$$\text{Using Maxwell's } \left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p \text{ and } \left(\frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T}$$

$$\frac{C_v}{T} = \left(\frac{C_p}{T} \left(\frac{\partial V}{\partial P} \right)_T + \left(\frac{\partial V}{\partial T} \right)_p^2 \right) / \left(\frac{\partial V}{\partial P} \right)_T \text{ so that}$$

$$C_p - C_v = -T \left(\frac{\partial V}{\partial T} \right)_p^2 / \left(\frac{\partial V}{\partial P} \right)_T = TV \alpha_p^2 / \kappa_T$$

Isothermal compressibility is defined as

$$\kappa_T \equiv - \frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

Compressibility in fluids does not contain any background, and the definition of the terms in the compressibility equation is based on

$$\tilde{\kappa}_T \equiv - \frac{V_c}{V} \frac{P_c}{V_c} \left(\frac{\partial V}{\partial P} \right)_T = - \frac{1}{\tilde{V}} \left(\frac{\partial \tilde{V}}{\partial \tilde{P}} \right)_T ???$$

$$\left(\frac{\partial \tilde{V}}{\partial \tilde{P}} \right)_T = - \left(a_{1eff} \left(\frac{\partial \phi_1}{\partial \tilde{P}} \right)_T + b_2 \left(\frac{\partial \phi_2}{\partial \tilde{P}} \right)_T \right)$$

$$\left(\frac{\partial \varphi_1}{\partial \tilde{P}}\right)_{\tilde{T}} = \frac{\partial \left(\varphi_1, \tilde{T}\right) / \partial (h_1, h_2)}{\partial \left(\tilde{P}, \tilde{T}\right) / \partial (h_1, h_2)} = \frac{\left(\frac{\partial \varphi_1}{\partial h_1}\right)_{h_2} \left(\frac{\partial \tilde{T}}{\partial h_2}\right)_{h_1} - \left(\frac{\partial \tilde{T}}{\partial h_1}\right)_{h_2} \left(\frac{\partial \varphi_1}{\partial h_2}\right)_{h_1}}{\left(\frac{\partial \tilde{P}}{\partial h_1}\right)_{h_2} \left(\frac{\partial \tilde{T}}{\partial h_2}\right)_{h_1} - \left(\frac{\partial \tilde{T}}{\partial h_1}\right)_{h_2} \left(\frac{\partial \tilde{P}}{\partial h_2}\right)_{h_1}}$$

$$\left(\frac{\partial \varphi_1}{\partial \Delta \tilde{P}}\right)_{\Delta \tilde{T}} = a_{1eff} \chi_1 + b_2 \chi_{12}$$

$$\left(\frac{\partial \varphi_2}{\partial \tilde{P}}\right)_{\tilde{T}} = \frac{\partial \left(\varphi_2, \tilde{T}\right) / \partial (h_1, h_2)}{\partial \left(\tilde{P}, \tilde{T}\right) / \partial (h_1, h_2)} = \frac{\left(\frac{\partial \varphi_2}{\partial h_1}\right)_{h_2} \left(\frac{\partial \tilde{T}}{\partial h_2}\right)_{h_1} - \left(\frac{\partial \tilde{T}}{\partial h_1}\right)_{h_2} \left(\frac{\partial \varphi_2}{\partial h_2}\right)_{h_1}}{\left(\frac{\partial \tilde{P}}{\partial h_1}\right)_{h_2} \left(\frac{\partial \tilde{T}}{\partial h_2}\right)_{h_1} - \left(\frac{\partial \tilde{T}}{\partial h_1}\right)_{h_2} \left(\frac{\partial \tilde{P}}{\partial h_2}\right)_{h_1}}$$

$$\left(\frac{\partial \varphi_2}{\partial \tilde{P}}\right)_{\tilde{T}} = a_2 \chi_{12} + b_2 \chi_2$$

and

$$\left(\frac{\partial \tilde{V}}{\partial \tilde{P}}\right)_{\tilde{T}} = -\left(a_{1eff}^2 \chi_1 + 2a_{1eff} b_2 \chi_{12} + b_2^2 \chi_2\right) = -\tilde{V} \tilde{\kappa}$$

$$\tilde{\kappa} = \frac{1}{\tilde{V}} \left(a_{1eff}^2 \chi_1 + 2a_{1eff} b_2 \chi_{12} + b_2^2 \chi_2\right)$$

The coefficient of thermal expansion is defined as

$$\alpha_P \equiv \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$$

$$\Delta \tilde{V} = \left(\frac{\partial \Delta \tilde{G}}{\partial \Delta \tilde{P}}\right)_{\Delta \tilde{T}} = -\left(a_{1eff} \varphi_1 + b_2 \varphi_2\right)$$

$$\left(\frac{\partial \tilde{V}}{\partial \tilde{T}}\right)_{\tilde{P}} = -\left(a_{1eff} \left(\frac{\partial \varphi_1}{\partial \tilde{T}}\right)_{\tilde{P}} + b_2 \left(\frac{\partial \varphi_2}{\partial \tilde{T}}\right)_{\tilde{P}}\right)$$

From the derivation for entropy:

$$\left(\frac{\partial \varphi_1}{\partial \Delta T} \right)_{\Delta P} = (a_2 \chi_1 + b_{1eff} \chi_{12})$$

and

$$\left(\frac{\partial \varphi_2}{\partial \Delta T} \right)_{\Delta P} = a_2 \chi_{12} + b_{1eff} \chi_2$$

and

$$\left(\frac{\partial \tilde{V}}{\partial \Delta T} \right)_{\Delta P} = - \left(a_{1eff} a_2 \chi_1 + (a_{1eff} b_{1eff} + a_2 b_2) \chi_{12} + b_{1eff} b_2 \chi_2 \right) = \tilde{V} \tilde{\alpha}$$

$$\tilde{\alpha}_P \equiv \frac{1}{\tilde{V}} \left(\frac{\partial \tilde{V}}{\partial \Delta T} \right)_{\Delta P} = - \frac{1}{\tilde{V}} \left(a_{1eff} a_2 \chi_1 + (a_{1eff} b_{1eff} + a_2 b_2) \chi_{12} + b_{1eff} b_2 \chi_2 \right)$$

III. Mean-Field or Classical Theory

The Landau expansion in powers of the order parameter φ_1

$$\Delta \tilde{G}(h_1, h_2) = \frac{1}{2} a_0 h_2 \varphi_1^2 + \frac{1}{4} u_0 \varphi_1^4 - h_1 \varphi_1$$

Minimizing the thermodynamic potential with respect to φ_1 yields

$$u_0 \varphi_1^3 + a_0 h_2 \varphi_1 - h_1 = 0$$

$$\varphi_2 = - \left(\frac{\partial \Delta \tilde{G}}{\partial h_2} \right)_{h_1} = - \frac{1}{2} a_0 \varphi_1^2$$

$$\chi_1 = \left(\frac{\partial h_1}{\partial \varphi_1} \right)_{h_2}^{-1} = \left(\frac{\partial (u_0 \varphi_1^3 + a_0 h_2 \varphi_1)}{\partial \varphi_1} \right)_{h_2}^{-1} = (3u_0 \varphi_1^2 + a_0 h_2)^{-1}$$

$$\chi_{12} = \left(\frac{\partial h_2}{\partial \varphi_1} \right)_{h_1}^{-1} = \left(\frac{\partial (u_0 \varphi_1^2 / a_0 - h_1 / a_0 \varphi_1)}{\partial \varphi_1} \right)_{h_2}^{-1} = \left(\frac{-2u_0 \varphi_1^3 - h_1}{a_0 \varphi_1^2} \right)^{-1} = \left(- \frac{a_0 \varphi_1^2}{2u_0 \varphi_1^3 + h_1} \right)$$

substituting for h_1 ,

$$\chi_{12} = \left(-\frac{a_o \varphi_1^2}{2u_o \varphi_1^3 + u_o \varphi_1^3 + a_o h_2 \varphi_1} \right) = \left(-\frac{a_o \varphi_1}{3u_o \varphi_1^2 + a_o h_2} \right) = -a_o \varphi_1 \chi_1$$

$$\begin{aligned} \chi_2 &= \left(\frac{\partial h_2}{\partial \varphi_2} \right)_{h_1}^{-1} = \left(\frac{\partial h_2}{\partial \varphi_1} \right)_{h_1}^{-1} \left(\frac{\partial \varphi_1}{\partial \varphi_2} \right)_{h_1}^{-1} \\ &= \left(\frac{\partial h_2}{\partial \varphi_1} \right)_{h_1}^{-1} \left(\frac{\partial \varphi_2}{\partial \varphi_1} \right)_{h_1} = \left(\frac{\partial h_2}{\partial \varphi_1} \right)_{h_1}^{-1} \left(\frac{\partial \left(-\frac{1}{2} a_o \varphi_1^2 \right)}{\partial \varphi_1} \right)_{h_1} = -a_o \varphi_1 \left(\frac{\partial h_2}{\partial \varphi_1} \right)_{h_1}^{-1} \end{aligned}$$

$$\partial \varphi_2 = \partial \left(-\frac{a_o \varphi_1^2}{2} \right) = -a_o \varphi_1 \partial \varphi_1$$

$$\chi_2 = \left(\frac{\partial h_2}{\partial \varphi_2} \right)_{h_2}^{-1} = -a_o \varphi_1 \left(\frac{\partial h_2}{\partial \varphi_1} \right)_{h_2}^{-1} = -a_o \varphi_1 \chi_{12} = a_o^2 \varphi_1^2 \chi_1$$

The critical part of the entropy,

$$\Delta \tilde{S} = - \left(a_2 \varphi_1 + b_{1eff} \varphi_2 \right) = \left(\frac{b_{1eff} a_o \varphi_1^2}{2} - a_2 \varphi_1 \right)$$

The heat capacity in classical theory is

$$\left(\frac{\partial \Delta \tilde{S}}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} = \left(b_{1eff} a_o \varphi_1 \left(\frac{\partial \varphi_1}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} - a_2 \left(\frac{\partial \varphi_1}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} \right) = \frac{\tilde{C}_p - \tilde{C}_p^r}{\tilde{T}}$$

Since

$$\left(\frac{\partial \varphi_1}{\partial \Delta \tilde{T}} \right)_{\Delta \tilde{P}} = \left(a_2 \chi_1 + b_{1eff} \chi_{12} \right) = \left(\frac{a_2 - a_o b_{1eff} \varphi_1}{a_o h_2 + 3u_o \varphi_1^2} \right)$$

we find

$$\Delta \tilde{C}_p = \frac{\tilde{T} \left(a_2 - a_o b_{1eff} \varphi_1 \right)^2}{\left(a_o h_2 + 3u_o \varphi_1^2 \right)}$$

$$\tilde{\kappa} = -\frac{1}{\tilde{V}} \left(\frac{\partial \tilde{V}}{\partial \tilde{P}} \right)_{\tilde{T}} = \frac{1}{\tilde{V}} \left(a_{1eff}^2 \chi_1 + 2a_{1eff} b_2 \chi_{12} + b_2^2 \chi_2 \right) = \frac{1}{\tilde{V}} \left(\frac{a_1^2 - 2a_{1eff} b_2 a_o \varphi_1 + b_2^2 a_o^2 \varphi_1^2}{3u_o \varphi_1^2 + a_o h_2} \right)$$

$$\begin{aligned} \tilde{\alpha}_P &\equiv \frac{1}{\tilde{V}} \left(\frac{\partial \tilde{V}}{\partial \tilde{\Delta T}} \right)_{\tilde{\Delta P}} = -\frac{1}{\tilde{V}} \left(a_{1eff} a_2 \chi_1 + (a_{1eff} b_{1eff} + a_2 b_2) \chi_{12} + b_{1eff} b_2 \chi_2 \right)_{\tilde{\Delta P}} \\ &= -\frac{1}{\tilde{V}} \left(\frac{a_{1eff} a_2}{(3u_o \varphi_1^2 + a_o h_2)} + (a_{1eff} b_{1eff} + a_{1eff} b_2) \left(-\frac{a_o \varphi_1^2}{2u_o \varphi_1^3 + h_1} \right) + \frac{b_2^2 a_o^2 \varphi_1^2}{(3u_o \varphi_1^2 + a_o h_2)} \right) \end{aligned}$$

Parametric Mean-Field Representation:

Using the simplest form of the parametric equations of state, we have a “linear model” for the “polar” variables r and θ .

$$h_1 = ar^{\beta+\gamma}\theta(1-\theta^2)$$

$$h_2 = r(1-b^2\theta^2)$$

$$\phi_1 = kr^\beta\theta$$

where r represents the distance to the critical point, θ is the distance along a contour of constant r , b is a universal constant, and a and k are system dependent constants.

In mean field (classical) theory, the magnitudes of the critical exponents are $\alpha = 0$,

$\beta = 1/2$, $\gamma = 1$, $\delta = \frac{\gamma}{\beta} + 1 = 3$, where δ is the universal critical exponent. The value

of $b^2 = (\gamma - 2\beta) / \gamma(1 - 2\beta)$ can be found by using the ε expansion for critical exponents, where $\varepsilon = 4 - d$. The mean field results are valid in the limit $\varepsilon \rightarrow 0$. In the first order of ε , the expansion gives $2\beta = 1 - \frac{1}{3}\varepsilon$, $\gamma = 1 + \frac{1}{6}\varepsilon$, $\alpha = \frac{1}{6}\varepsilon$, thus $b^2 = 3/2$.

For scaling densities and susceptibilities in the parametric form:

$$\phi_1 = kr^{1/2}\theta$$

$$\phi_2 = -\frac{1}{2}akr\theta^2 = -\frac{1}{2}a_0\phi_1^2$$

$$\chi_1 = (k/a)r^{-1} = [a_0h_2 + 3u_0\phi_1^2]^{-1}$$

$$\chi_{12} = -kr^{-1/2}\theta = -a_0\phi_1\chi_1$$

$$\chi_2 = ak\theta^2 = \frac{a_0^2}{2u_0}\theta^2 = a_0^2\phi_1^2\chi_1$$

where the coefficients are related to k and a as follows:

$$a_0 = a/k$$

$$u_0 = a/2k^3$$

$$ak = a_0^2/2u_0$$

IV. Scaling Theory and the Parametric Linear Model

Equations of state described through power laws are called “scaling laws”. They are characterized by universal exponents or critical exponents. In scaling theory these exponents have values:

Critical Exponent	Scaling Theory	Mean-Field Theory
α	0.11 +/- 0.01	0
β	0.325 +/- 0.005	0.5
δ	4.81	3
γ	1.24 +/- 0.01	1
b^2	1.36	1.5
ϑ	1.26 +/- 0.02	1.5 in vdw
ν	0.63 +/- 0.01	Not defined unambiguously

Delta is the universal critical exponent, found from the relation $(\delta - 1)\beta = \gamma$.

The simplest form of the parametric equations of state is the “linear model”, representing h_1 and h_2 using the “polar variables” r and θ .

$$h_1 = ar^{\beta+\gamma}\theta(1-\theta^2)$$

$$h_2 = r(1-b^2\theta^2)$$

The singular part of the thermodynamic potential is:

$$\Delta\tilde{\Phi}(r,\theta) = akr^{2-\alpha}\left[f(\theta) - \theta^2(1-\theta^2)\right] + (ak/6)r^2(1-b^2\theta^2)^2$$

with the last term added to make the model fully consistent with the results of renormalization group (RG) theory².

$$\varphi_1 = kr^\beta\theta, \quad \varphi_2 = akr^{1-\alpha}s(\theta) - akr(1-b^2q^2)/3$$

$$\chi_1 = \left(\frac{k}{a}\right)r^{-\gamma}c_1(\theta)$$

$$\chi_{12} = kr^{\beta-1}c_{12}(\theta)$$

$$\chi_2 = akr^{-\alpha}c_2(\theta) - ak/3$$

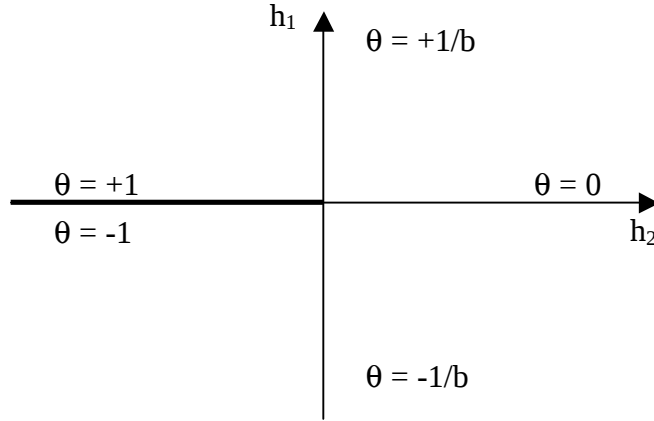
where r represents the distance to the critical point, the parameter θ is the distance along a contour of constant r , the coefficient $b^2 = (\gamma - 2\beta) / \gamma(1 - 2\beta)$ is a universal constant, and a and k are system dependent constants.

The universal heat capacity is given as:

$$C_p = -T\left(a_2^2\chi_1 + 2a_2b_{1eff}\chi_{12} + b_{1eff}^2\chi_2\right) + C_p^r$$

² M.A. Anisimov, V.A. Agayan, P.J. Collings, “Nature of the Blue-Phase-III-Isotropic...”

The polar variables r and q used in the parametric representation of the equation of state are shown below.



The functions $f(\theta)$, $s(\theta)$, and $c_i(\theta)$ are known functions of θ :

$$f(\theta) = f_0 + f_2\theta^2 + f_4\theta^4$$

$$f_0 = -\frac{\beta(\delta-3) - b^2\alpha\gamma}{2b^4(2-\alpha)(1-\alpha)\alpha}$$

$$f_2 = \frac{\beta(\delta-3) - b^2\alpha(1-2\beta)}{2b^2(1-\alpha)\alpha}$$

$$f_4 = -\frac{1-2\beta}{2\alpha}$$

$$s(\theta) = s_0 + s_2\theta^2$$

$$s_0 = -(2-\alpha)f_0$$

$$s_2 = -(2-\alpha)b^2(1-2\beta)f_0 - \gamma f_2$$

$$c_1(\theta) = (1 - b^2\theta^2(1-2\beta)) / (c_0(\theta))$$

$$c_{12}(\theta) = \beta\theta[1 - \delta - \theta^2(3 - \delta)] / c_0(\theta)$$

$$c_0(\theta) = (1 - 3\theta^2)(1 - b^2\theta^2) + 2\beta\delta b^2\theta^2(1 - \theta^2)$$

To solve for thermodynamic properties for water at the critical pressure using the scaling theory, we find:

$$h_1 = a_2\Delta\tilde{T} = ar^{\beta+\gamma}\theta(1-\theta^2)$$

$$h_2 = b_1\Delta T = r(1-b^2\theta^2)$$

Rearranging and combining terms:

$$\frac{ar^{\beta+\gamma}\theta(1-\theta^2)}{a_2} = \frac{r(1-b^2\theta^2)}{b_1}$$

$$r = \left(\frac{a_2 r (1-b^2\theta^2)}{ab_1\theta(1-\theta^2)} \right)^{(1/(\beta+\gamma-1))} . \text{ Given theta, r and } \Delta\tilde{T} \text{ are well defined.}$$

To solve for thermodynamic properties for water at any pressure using the scaling theory, we find:

$$h_1 = a_1\Delta\tilde{P} + a_2\Delta\tilde{T} + a_3\Delta\tilde{P}^2 = ar^{\beta+\gamma}\theta(1-\theta^2)$$

$$h_2 = b_1\Delta\tilde{T} + b_2\Delta\tilde{P} = r(1-b^2\theta^2).$$

Rearranging and combining terms:

$$r^{\beta+\gamma} \frac{a\theta(1-\theta^2)}{a_2} + r \frac{(b^2\theta^2-1)}{b_1} = -\frac{b_2}{b_1}\Delta\tilde{P} + \frac{a_1}{a_2}\Delta\tilde{P} + \frac{a_3}{a_2}\Delta\tilde{P}^2$$

of the form $Ar^{\beta+\gamma} + Br = C$

OR

$$-\frac{a_1\Delta\tilde{P}}{a_2} - \frac{a_3\Delta\tilde{P}^2}{a_2} + \frac{ar^{\beta+\gamma}\theta}{a_2} - \frac{ar^{\beta+\gamma}\theta^3}{a_2} = \Delta\tilde{T}$$

$$\frac{r}{b_1} - \frac{rb^2}{b_1}\theta^2 - \frac{b_2\Delta\tilde{P}}{b_1} = \Delta\tilde{T}$$

$$-\frac{ar^{\beta+\gamma}}{a_2}\theta^3 + \frac{rb^2}{b_1}\theta^2 + \frac{ar^{\beta+\gamma}}{a_2}\theta + \frac{b_2\Delta\tilde{P}}{b_1} - \frac{r}{b_1} - \frac{a_1\Delta\tilde{P}}{a_2} - \frac{a_3\Delta\tilde{P}^2}{a_2} = 0$$

in the form of $Ax^3 + Bx^2 + Cx + D = 0$

where

$$A = -\frac{ar^{\beta+\gamma}}{a_2}, B = \frac{rb^2}{b_1}, C = \frac{ar^{\beta+\gamma}}{a_2}, D = \frac{b_2\Delta\tilde{P}}{b_1} - \frac{r}{b_1} - \frac{a_1\Delta\tilde{P}}{a_2} - \frac{a_3\Delta\tilde{P}^2}{a_2}$$

Substituting $y = x + \frac{B}{3A}$, we get $y^3 + 3Py + Q = 0$

$$\text{Where } P = \frac{3AC - B^2}{9A^2} \text{ or } P = -\left(\frac{1}{3} + \frac{1}{9} \left(\frac{ra_2b^2}{b_1ar^{\beta+\gamma}} \right)^2 \right)$$

and $Q = \frac{2B^3 - 9ABC + 27A^2D}{27A^3}$ or

$$Q = \frac{2\left(\frac{rb^2}{b_1}\right)^3 + 9\left(\frac{ar^{\beta+\gamma}}{a_2}\right)^2\left(\frac{rb^2}{b_1}\right) + 27\left(\frac{ar^{\beta+\gamma}}{a_2}\right)^2\left(\frac{b_2\Delta\tilde{P}}{b_1} - \frac{r}{b_1} - \frac{a_1\Delta\tilde{P}}{a_2} - \frac{a_3\Delta\tilde{P}^2}{a_2}\right)}{-27\left(\frac{ar^{\beta+\gamma}}{a_2}\right)^3} \quad \text{or}$$

$$Q = -\frac{2}{27}\left(\frac{a_2rb^2}{ar^{\beta+\gamma}b_1}\right)^3 - \frac{1}{3}\left(\frac{a_2rb^2}{ar^{\beta+\gamma}b_1}\right) - \left(\frac{a_2}{ar^{\beta+\gamma}}\right)\left(\frac{b_2\Delta\tilde{P}}{b_1} - \frac{r}{b_1} - \frac{a_1\Delta\tilde{P}}{a_2} - \frac{a_3\Delta\tilde{P}^2}{a_2}\right)$$

Defining

$$\alpha = \frac{-Q + \sqrt{Q^2 + 4P^3}}{2} \quad \text{and} \quad \beta = \frac{-Q - \sqrt{Q^2 + 4P^3}}{2}$$

The solution to the equation $y^3 + 3Py + Q = 0$ is given by

$$\sqrt[3]{\alpha} + \sqrt[3]{\beta}, \quad e^{\frac{2\pi i}{3}}\sqrt[3]{\alpha} + e^{\frac{4\pi i}{3}}\sqrt[3]{\beta}, \quad e^{\frac{4\pi i}{3}}\sqrt[3]{\alpha} + e^{\frac{2\pi i}{3}}\sqrt[3]{\beta}.$$

Since $e^{ix} = \cos x + i \sin x$,

$$e^{\frac{i4\pi}{3}} = \cos\left(\frac{4\pi}{3}\right) + i \sin\left(\frac{4\pi}{3}\right) = -\frac{1}{2} - i\frac{\sqrt{3}}{2}, \quad e^{\frac{i2\pi}{3}} = \cos\left(\frac{2\pi}{3}\right) + i \sin\left(\frac{2\pi}{3}\right) = -\frac{1}{2} + i\frac{\sqrt{3}}{2}$$

Using this, the solution

$$e^{\frac{2\pi i}{3}}\sqrt[3]{\alpha} + e^{\frac{4\pi i}{3}}\sqrt[3]{\beta} = -\frac{1}{2}\sqrt[3]{\alpha} + i\frac{\sqrt{3}}{2}\sqrt[3]{\alpha} - \frac{1}{2}\sqrt[3]{\beta} - i\frac{\sqrt{3}}{2}\sqrt[3]{\beta} = -\frac{1}{2}(\sqrt[3]{\alpha} + \sqrt[3]{\beta}) + i\frac{\sqrt{3}}{2}(\sqrt[3]{\alpha} - \sqrt[3]{\beta})$$

V. Actual EOS Equations:

Solving for theta, $h_1 = (a_1)_{\text{eff}} \Delta P + a_2 \Delta T = ar^{\beta+\gamma} \theta (1 - \theta^2)$, from scaling theory

We simplify the equation and get $ar^{\beta+\gamma} \theta^3 - ar^{\beta+\gamma} \theta + ((a_1)_{\text{eff}} \Delta P + a_2 \Delta T) = 0$ in the form

of $ax^3 + bx^2 + cx + d = 0$. Substituting $y = x + \frac{b}{3a}$, we get the equation

$y^3 + 3py + q = 0$, where $p = \frac{3ac - b^2}{9a^2}$ and $q = \frac{2b^3 - 9abc + 27a^2d}{27a^3}$. The discriminant of

this polynomial is $4p^3 + q^2$. The solutions are given by $\sqrt[3]{\alpha} + \sqrt[3]{\beta}$, $e^{\frac{2\pi i}{3}} \sqrt[3]{\alpha} + e^{\frac{4\pi i}{3}} \sqrt[3]{\beta}$,

and $e^{\frac{4\pi i}{3}} \sqrt[3]{\alpha} + e^{\frac{2\pi i}{3}} \sqrt[3]{\beta}$, where $\alpha = \frac{-q + \sqrt{q^2 + 4p^3}}{2}$ and $\beta = \frac{-q - \sqrt{q^2 + 4p^3}}{2}$. If the

discriminant is +, then 1 root is real and 2 are complex conjugates. If the discriminant is 0, then there are 3 real roots of which at least two are equal. If the discriminant is negative, then there are 3 unequal real roots.

$$\text{Column C: } \theta^3 = -\frac{a \cdot r^{\beta+\gamma}}{a_2}$$

$$\text{Column D: } \theta^2 = \frac{r \cdot b^2}{(b_1)_{\text{eff}}}$$

Column E: has b1eff for Column D equation and ??

$$\text{Column F: } \theta^1 = \frac{a \cdot r^{\beta+\gamma}}{a_2}$$

$$\text{Column G: } \theta^0 = -\frac{a_3 \cdot \Delta P^2}{a_2} - \frac{(a_1 + 2a_3 \Delta P) \Delta P}{a_2} + \frac{b_2 \Delta P}{(b_1)_{\text{eff}}} - \frac{r}{(b_1)_{\text{eff}}}$$

$$\text{Column H: } P = \frac{3 \cdot \theta^3 \cdot \theta^1 - (\theta^0)^2}{9 \cdot \theta^3}$$

$$\text{Column I: } Q = \frac{2 \cdot (\theta^2)^3 - 9 \cdot \theta^3 \cdot \theta^2 \cdot \theta + 27 \cdot (\theta^3)^2 \theta^0}{27 \cdot (\theta^3)^3}$$

$$\text{Column J: } Q^2 + 4P^3$$

Column K: IF $Q^2 + 4P^3 = 0$, then $\alpha = -\frac{Q}{2}$. If not, then if $Q^2 + 4P^3 > 0$,

$$\alpha = \frac{-Q + \sqrt{Q^2 + 4P^3}}{2}. \text{ If } Q^2 + 4P^3 < 0, \text{ then } \alpha = -\frac{Q}{2} + \frac{\sqrt{Q^2 + 4P^3}}{2}i$$

Column L: If $Q^2 + 4P^3 = 0$, then $\beta = -\frac{Q}{2}$. If not, then if $Q^2 + 4P^3 > 0$,

$$\beta = \frac{-Q - \sqrt{Q^2 + 4P^3}}{2}. \text{ If } Q^2 + 4P^3 < 0, \text{ then } \beta = -\frac{Q}{2} - \frac{\sqrt{Q^2 + 4P^3}}{2}i$$

$$\text{Column M: Solution1} = \alpha^{1/3} + \beta^{1/3}$$

$$\text{Column N: Solution2} = \alpha^{1/3}e^{2\pi i/3} + \beta^{1/3}e^{4\pi i/3}$$

$$\text{Column O: Solution3} = \alpha^{1/3}e^{4\pi i/3} + \beta^{1/3}e^{2\pi i/3}$$

$$\text{Column P: } \theta_1 = \alpha^{1/3} + \beta^{1/3} - \frac{(\theta^2)}{3(\theta^3)}$$

$$\text{Column Q: } \theta_2 = \alpha^{1/3}e^{2\pi i/3} + \beta^{1/3}e^{4\pi i/3} - \frac{(\theta^2)}{3(\theta^3)}$$

$$\text{Column R: } \theta_3 = \alpha^{1/3}e^{4\pi i/3} + \beta^{1/3}e^{2\pi i/3} - \frac{(\theta^2)}{3(\theta^3)}$$

Using theta to solve for thermodynamic properties and the critical point

$$\text{Column S: } \Delta T = \frac{r(1 - b^2\theta^2)}{(b_1)_{\text{eff}}} - \frac{\Delta P b_2}{(b_1)_{\text{eff}}}$$

$$\text{Column T: } T = \frac{\Delta T \cdot T_c}{T_c}$$

$$\text{Column U: } h_1 = a_1\Delta P + a_2\Delta T + a_3\Delta P^2$$

$$\text{Column V: } h_2 = b_1\Delta T + b_2\Delta P + b_3\Delta T^2$$

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