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**CRYSTALLIZATION, LIQUID-LIQUID PHASE TRANSITION  
AND RELAXATION IN SUPERCOOLED WATER**

by

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**CRYSTALLIZATION, LIQUID-LIQUID PHASE TRANSITION  
AND RELAXATION IN SUPERCOOLED WATER**

(Order No.           )

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Boston University Graduate School of Arts and Sciences, 2003

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We investigate supercooled water to understand the origins of its anomalies. We study for the first time many properties of the “transferable intermolecular potential with five points” model (TIP5P), a rigid, non-polarizable water model parameterized to match the properties of real water. TIP5P is the only model that exhibits spontaneous nucleation within a reasonable time, enabling us to calculate an “optimum” temperature at which it freezes fastest. The existence of a minimum freezing time is consistent with experiments on aqueous solutions, but has not been seen before in pure water simulations or experiments due to technical difficulties. We also study supercooled water prior to freezing, and find evidence of a liquid-liquid critical point, supporting previously-proposed theory to explain water anomalies. We also find that the temperature dependence of the dynamics of mildly supercooled TIP5P water follows the predictions of the idealized mode-coupling theory (MCT). All calculations using the TIP5P model are in quantitative agreement with experiment, suggesting that the model may be used for explanatory and predictive work on real supercooled water.

Next, we use a well-known classical water model developed by Stillinger and Rahman to compare a novel simulation method with those in the literature. It is difficult to observe a liquid-liquid phase transition using standard simulation methods, since the creation of two distinct liquid phases is hampered by finite-size effects. By plac-

ing a simulation system in a gravitational field and calculating the density profile, an equation of state can be calculated and an interface between two liquid states can be seen. We show that our calculated pressures are equivalent to values calculated by others using the virial expansion method.

Finally, to gain a deeper understanding of water anomalies, we develop a model with tunable parameters that enables us to continuously progress from a spherically symmetric model, to one with independent hydrogen-bonding arms, to one where the arms possess intramolecular correlation. We show how each parameter affects the properties of liquid “water” such as the density anomaly, the fluid-fluid phase transition, and the second critical point.

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# List of Abbreviations

TIP5P	Transferable Intermolecular Potential with Five Points
ST2	No particular meaning
TTT	Time-Temperature-Transformation curves
HB	Hydrogen Bond
RDF	Radial Distribution Function
MCT	Mode Coupling Theory
EOS	Equation of State
MD	Molecular Dynamics simulation
MC	Monte Carlo simulation
MF	Mean Field calculation
NPT	Constant number, pressure, temperature

## Chapter 1

# Introduction

### 1.1 Interest in Supercooled Liquid Water

Given the ubiquity and importance of water in our daily lives, it is perhaps not surprising that a considerable body of literature is committed to addressing this substance[1–4]. Water, also known as “blue gold,” is an element that is common to mythology, philosophy, sociology, agriculture, meteorology, literature and other fields.

Water possesses many scientific properties that make it stand out among liquids. It has an extraordinary number of phases – nearly twenty if the metastable phases are included – and is one of the few pure substances where different phases can be seen even under everyday conditions. The density maximum at 4 degrees Celsius (at atmospheric pressure) prevents under-water life from freezing in the winter. Its high heat capacity gives it the capability to prevent extreme swings in temperature on Earth. Its tetrahedral shape and distribution of charges enables it to be the so-called “universal” solvent.

Many of these special properties of water, both static and dynamic, exhibit diverging behavior as temperature is lowered below the melting line. Examples of equilib-



rium quantities that apparently diverge include: isothermal compressibility, density, and heat capacity. Dynamic quantities such as diffusion constant and translation and rotational relaxation times also seem to diverge at a singular temperature.

It is not possible to observe the diverging behavior directly because the water cannot be supercooled to low enough temperatures; inevitable crystallization occurs below the homogeneous nucleation temperature. However, extrapolations from the liquid regime indicate that around  $-45\text{ C}^\circ$  at atmospheric pressures, there is some kind of “critical temperature.” This temperature is related to the singular behavior seen in so many water properties.

The question is what mechanism gives rise to this singular behavior. Through the course of this dissertation research, our goal has been to understand the anomalous properties of liquid water by addressing its behavior in the supercooled region. Three scenarios have been proposed so far to explain the divergent temperature:

1. Stability Limit Conjecture, where the anomalies are attributed to a spinodal line in the supercooled region of water, near the singularity temperature. This spinodal is a continuous extension of the liquid-gas spinodal[5].
2. Second Critical Point Scenario, where the anomalies are attributed to a liquid-liquid critical point in the supercooled regime (the critical point obscured by spontaneous crystallization, but its effects far-reaching)[6, 7].
3. Singularity Free Scenario, where no thermodynamic instabilities such as a spinodal line or critical point are necessary to produce anomalous behavior seen in liquid water, and where the supercooled properties never diverge at all[8–12].

There has still not been a conclusive answer, given the difficulty of performing both simulations and experiments in this supercooled regime. In this thesis, we perform

simulations using new models and new methods not used in the past, and add to the body of evidence that would point to one (the correct) answer.

## 1.2 Our Simulation Studies

We use three different water models in this thesis: the transferable intramolecular potential with five points (TIP5P)[13], the ST2 potential[14], and our own idealized potential[15].

The TIP5P and ST2 potentials are both pair-wise additive, rigid, non-polarizable potentials with 5 interaction sites. Their differences are subtle, with just slight changes in the geometry and charges places on each of the sites.

Our own potential is one that attempts to distill the important qualities of a “water-like” potential in order to understand which features give rise to particular properties of water.

We use a different simulation method for these models. For the TIP5P model, we perform standard molecular dynamics simulations in the microcanonical ensemble. For the ST2 model, we perform molecular dynamics simulation using the sedimentation equilibration method. For the simulations using our own potential, we use the constant pressure, constant volume ( $NPT$  ensemble) Monte Carlo method. Each simulation method has been chosen to best fit our motive.

Obviously, the quality of our work is limited by the quality of the models and the effectiveness of the simulation method employed. Part of the reason we use these different methods is to see whether they lead to the same answer with regards the cause of the anomalies of water.

Our particular motivations for performing each of these studies are:

- When compared to experimental data at room temperature and atmospheric

pressure, TIP5P has been shown to have the closest structural, thermodynamic, and dynamic behavior of all classic water potentials. It also shows pressure and temperature dependence away from the region in which it was calibrated [13, 16]. A relatively new potential, its properties in the supercooled regime have not been extensively studied. Given its quantitative agreement with real water under ambient conditions, our desire has been to use this model to evaluate, explain and predict the behavior of *real* water. We also use this potential to test mathematical theories on liquids such as the mode-coupling theory (MCT) [17]. We perform “standard” molecular dynamics simulations, where each simulation box has an externally defined density, temperature, and number of particles. This enables us to study each state point independently to observe its qualities. Molecular dynamics allows us to study both thermodynamic and dynamic behavior; Monte Carlo methods can also be used for equilibrium studies.

- ST2 is a well-known water potential that has been extensively studied by others, including in the supercooled regime. We use this potential to test a novel simulation method to see whether it is effective in the study of liquid-liquid phase coexistence. Since we are employing a new simulation method, we decided to use an established model, so we could compare our results to results already in the literature.

We use the sedimentation equilibration method in order to see liquid-liquid coexistence directly, with an interface in between two phases. Simulating phase equilibria is a difficult task, especially for dense liquids, and we show that this method facilitates this task.

- We develop our own idealized potential to try to extract the relevant features of a model – the minimum number of features – to reproduce all of the anoma-

lies of water. There exist many idealized potentials that replicate some of the properties of water, but none of the simple models can replicate all of them. Our idealized model has parameters that can be tuned continuously to replicate many of the existing simple water-like models, thus enabling us to determine the effect of each of the parameters on the behavior of water.

We perform mean-field calculations to find the overall properties of our model. We then perform Monte Carlo simulations to take into account thermal fluctuations. Because we put “spin” states on each of the particles to model the rotational orientation of water molecules, it is not feasible to perform molecular dynamics simulations in this situation. We choose a constant pressure ensemble because it allows density fluctuations, and mimics experimental conditions.

Although the results of simulation studies must be validated by experimental proof, there are some known advantages to simulations over experiment.

For example, in our study on the crystallization of supercooled TIP5P water in Chapter 2, we are able to cool water at an arbitrarily fast rate; so quickly that we can avoid spontaneous nucleation. It is technically unfeasible to quench a system so rapidly under experimental conditions. In addition, it is difficult to make a real system infinitely clean, making the study of spontaneous nucleation difficult. Simulations can avoid these purely technical difficulties.

Models have also been instructive in distilling the relevant features that give rise to certain behaviors in real systems. For example, one question that has been raised is whether the well-known temperature of maximum density in water is related to the liquid-liquid phase transition in the supercooled water regime, since the thermal expansion coefficient is one of the many quantities that would apparently diverge in the supercooled regime, if metastable liquid water could be supercooled indefinitely.

Many simple “water-like” models have developed to test what gives rise to these phenomena[11,18–23]. and it has been shown that these qualities can be mutually exclusive: density maxima have been produced in models in the absence of a liquid-liquid phase transition, and liquid-liquid phase transitions have been seen using potentials that do not produce density maxima. However, it is also the case that both features have been seen simultaneously using a very simple spherical model; the existence of a liquid-liquid transition is controlled by simply tuning the interaction strength and range[24].

Through these simple models, it has been found that central to the effectiveness of these toy water models is one unifying feature: the model must have two possible “bonding states.” One of the states is a high density, high energy, high entropy state (non-hydrogen bonded) and the other is a lower density, lower energy, lower entropy state (hydrogen bonded). The competition between potential energy and entropy is said to give rise to many of the interesting phenomena seen in water.

Although it is encouraging to see many liquid water anomalies using simple models, none of these potentials has produced all of the features seen in water; for instance, replicating the fluid-fluid phase transition line with the correct negative slope in the pressure-temperature phase diagram has been a feat thus far not accomplished using isotropic models. Thus, although these potentials are called “water-like,” they still cannot be used for predictive studies of real water.

We created our tunable potential because the relative importance of the different features has not been made clear in existing models. Indeed, both the Sastry[11] and the Jagla models[24] show a density maximum with no liquid-liquid phase transition, but the Sastry model is a lattice model (with no local density fluctuations) that has directional hydrogen bonding arms with a “rotational” degree of freedom, while the Jagla potential is continuous one that is completely spherical. Other such cases

abound. Our potential has tunable parameters that enable us to move from one scenario to another. We can also observe the effect of adding another degree of freedom: the effect of “internal” coordination and the hydrogen-bonding arms.

## Chapter 2

# Thermodynamic Properties of Supercooled TIP5P Water

## 2.1 Background

Much effort has been invested in exploring the overall phase diagram of water and the connection among its liquid, supercooled and glassy states [2, 7, 25], with particular interest in understanding the origin of the striking anomalies at low temperatures, such as the  $T$ -dependence of the isothermal compressibility  $K_T$ [26], the constant pressure specific heat  $C_P$ [27], and the thermal expansivity  $\alpha_P$ [28]. In the previous chapter, we have introduced the three scenarios proposed to explain these anomalies.

We perform molecular dynamics simulations of TIP5P water[13] in order to investigate the properties of supercooled liquid water. “Equilibrium” simulations of supercooled metastable states are possible because the structural relaxation time at the temperatures of interest is several orders of magnitude shorter than the crystallization time. It is difficult, but not impossible [29], to observe crystallization in simulations of molecular models [30] because homogeneous nucleation rarely occurs on the time scales reachable by present day computers. Bulk water simulations have been crystallized by applying a homogeneous electric field [31] or placing liquid wa-

ter in contact with pre-existing ice [32, 33], but spontaneous crystallization of deeply supercooled model water has not been observed in simulations.

In contrast, experimental measurements of metastable liquid states are strongly affected by homogeneous nucleation. The nucleation and growth of ice particles from aqueous solution has been extensively studied, and the “nose-shaped” time-temperature-transformation (TTT) curves have been measured [2, 34, 35]. The non-monotonic relation between crystallization rate and supercooling depth results from the competition between the thermodynamic driving force for nucleation and the dynamics of growth [2]. Crystallization hinders direct experimental investigation of pure metastable liquid water below the homogeneous nucleation line; only indirect measurements can be made by studying the metastable melting lines of ices [7].

This work attempts to unify the phenomena connected with the existence of a liquid-liquid phase transition and homogeneous nucleation in a single molecular dynamics simulation study.

## 2.2 Introduction

The TIP5P is closer to real water than previously-proposed classical pairwise additive potentials[13]. In this chapter, we primarily focus on thermodynamic properties; we will extend our analysis into the dynamical properties in the chapter that follows.

A relatively new potential, this is the first extensive study of deeply supercooled TIP5P water. We simulate a system of 343 TIP5P molecules in a wide range of deeply supercooled states and present four main results regarding the properties of supercooled TIP5P water:

1. The existence of a non-monotonic “nose-shaped” temperature of maximum density line and a non-reentrant spinodal.



2. The presence of a low temperature liquid-liquid phase transition
3. The free evolution of bulk water to ice
4. Time-temperature-transformation curves at different densities

The first point supports previous simulation and experimental results *against* the “re-entrant spinodal” theory. The second point supports previous simulation and experimental results *for* the “second critical point” theory that attributes water anomalies to a thermodynamic singularity in the deeply supercooled region. This theory is still under debate, given the difficulty of probing this region via experiments and simulations. However, our results using this new water model supports this theory.

The third point is interesting in that it is extremely rare to see spontaneous nucleation in simulations of water: we know of only one other published study that claims to see the free evolution of bulk water to ice (this work took seven years of simulation time). Indeed, it is difficult to see spontaneous nucleation of many simulation substances, in part because current computers allow simulations of this type to run for, at best, on the order of milliseconds. In addition, finite-size effects severely hamper phase transitions.

The fourth point is a true first in this field: the time-temperature-transformation (TTT) curves have never been seen in water simulations. Indeed, TTT curves for homogeneous nucleation in pure water are very difficult to see even experimentally, because of the technical difficulties of keeping the apparatus clean, and determining the spontaneous crystallization time. TTT curves *have* been seen for water solutions with different concentrations of solutes. The solutes hamper too-quick freezing, and as the concentration decreases, the TTT curves are seen on shorter time scales; these results can be extrapolated to estimate the shape of the TTT curve when the concentration of solute is zero.

## 2.3 Correspondence Between Simulation and Experimental Values

It has been previously shown that near ambient conditions, the TIP5P water potential possesses structural, thermodynamic and dynamics characteristics in *quantitative* agreement with real water. In order to verify the correspondence between calculated quantities in TIP5P water and known quantities in real water far away from ambient conditions, we calculate the location of the (well known) liquid-gas critical point using TIP5P water to “pin down” another reference point with respect to real water.

Fig. 2.1 shows the equation of state of TIP5P water near the liquid-gas critical point. A clear inflection is seen in the equation of state below temperature  $T = 525K$ . The coordinates of the liquid-gas critical point for the TIP5P model are:  $\rho = 0.33g/cm^3$ ,  $T = 530K$ ,  $P = 10MPa$ . The experimental values are:  $\rho = 0.322g/cm^3$ ,  $T = 646K$ , and  $P = 22MPa$ .

The critical density and critical pressure are in reasonable agreement with experimental values, but the temperature we calculate is over 100 degrees lower. This is not surprising given that Mahoney and Jorgensen center their parameterization about the temperature of maximum density at atmospheric pressure (which is in quantitative agreement with experiment) with the caveat that the entire “envelope” that bounds the behavior of TIP5P water as a function of pressure and temperature has a steeper dependence than in real water. Specifically, they note that the slope of density as a function of temperature is much steeper at temperatures above ambient temperatures than at temperatures below. This means that the high temperature part of the TIP5P phase diagram is expected to be squeezed into a narrower (and hence lower) range of temperatures. This is confirmed by the location of the liquid-gas critical point; in real water, it is located about 400 degrees above the temperature of maximum density,

but in TIP5P water, it is shifted about 100 degrees down.

Mahoney and Jorgensen point out that as temperature is lowered below ambient temperatures, the envelope is also steeper than in experiment, but they say the discrepancy is far less severe than for the higher temperature region. In any case, the high temperature critical point, hundreds of degrees above the temperature of maximum density, shows only a 20 percent shift; our supercooled studies only go about 50 degrees below the temperature of maximum density, so if anything, we are encouraged that any property we measure in the supercooled region of TIP5P water is likely to be shifted only a few percent *higher* in temperature than in real water.

This asymmetry in the temperature-dependence of the TIP5P model (compared to experiment) is not unexpected, since it is difficult to calibrate water potentials. However, it is important that we understand how much the phase diagram is skewed because of this. The degree of skewing is not uniform over the entire phase diagram. Thus, the common practice of shifting simulation temperatures and pressures by constant values to reflect the estimated experimental temperatures is to be doubted. It is common to linearly “translate” the entire phase diagram calculated by simulation by a constant temperature or pressure to estimate analogous experimental values. However, this simple comparison using TIP5P shows that it is not possible to simply shift the phase diagram by constant values to obtain the correct mapping between simulation and experimental coordinates.

It not often that even one state point of a simulation model is in quantitative agreement with experiment, and the TIP5P water model has shown itself superior to other potentials in this regard.

## 2.4 Simulation and Results

We perform equilibration runs at constant  $T$  (see Appendix for Berendsen’s thermostat), while we perform production runs in the microcanonical (NVE) ensemble. After thermalization at  $T = 320$  K we set the thermostat temperature to the temperature of interest. We let the system evolve for a time longer than the structural relaxation time  $\tau_\alpha$ , defined as the time at which  $F_s(Q_0, \tau_\alpha) = 1/e$ , where  $F_s(Q_0, t)$  is the self-intermediate scattering function evaluated at  $Q_0 = 18 \text{ nm}^{-1}$ , the location of the first peak of the static structure factor. In the time  $\tau_\alpha$ , each molecule diffuses on average a distance of the order of the nearest neighbor distance. We use the final configuration of the equilibration run to start a production run of length greater than several  $\tau_\alpha$  and then analyze the calculated trajectory. We check that no drift in any of the studied quantities and no crystallization occurs during the production run.

In Fig. 2.2 we show results for pressure along isotherms. At lower temperatures an inflection develops, which becomes a “flat” isotherm at the lowest temperature,  $T = 215$  K. The presence of a flat region indicates that a phase separation takes place, and we estimate the critical temperature  $T_{C'} = 217 \pm 3$  K, the critical pressure  $P_{C'} = 340 \pm 20$  MPa, and the critical density  $\rho_{C'} = 1.13 \pm 0.04 \text{ g/cm}^3$ .

In Fig. 2.3(a) we plot the pressure along isochores. The curves show minima as a function of temperature; the locus of the minima is the TMD line, since  $(\partial P/\partial T)_V = \alpha_P/K_T$ . It can be seen that the pressure exhibits a minimum if the density passes through a maximum ( $\alpha = 0$ ). It is clear that, as in the case of ST2 water, TIP5P water has a TMD that changes slope from negative to positive as P decreases. Notably, the point of crossover between the two behaviors is located at ambient pressure,  $T \approx 4$  C, and  $\rho \approx 1 \text{ g/cm}^3$ .

We also plot the spinodal line. We calculate the points on the spinodal line fitting

the isotherms (for  $T \geq 300K$ ) of Fig. 2.2 to the form  $P(T, \rho) = P_s(T) + A [\rho - \rho_s(T)]^2$ , where  $P_s(T)$  and  $\rho_s(T)$  denote the pressure and density of the spinodal line. This functional form is the mean field prediction for  $P(\rho)$  close to a spinodal line. For  $T \leq 250K$ , we calculate  $P_s(T)$  by estimating the location of the minimum of  $P(\rho)$ . The results in Fig.2.3 show that the liquid spinodal line is not reentrant and does not intersect the TMD line [36].

A supercooled liquid is metastable with respect to the crystal, so it is driven to crystallize [2]. However, crystallization of model water has not been found in simulations because the homogeneous nucleation time far exceeds the CPU time. However, for TIP5P, crystallization times lie within a time window accessible to present-day simulations, and we observe crystallization at densities  $\rho = 1.15 \text{ g/cm}^3$ , and  $1.20 \text{ g/cm}^3$  for a wide range of temperatures (Fig. 2.5). To quantify the crystallization process, we analyze four independent configurations thermalized at temperature  $T = 320 \text{ K}$  and instantaneously quenched to the temperature of interest. We monitor the potential energy as well as the time evolution of the structure factor  $S_{\vec{Q}}(t) \equiv \langle \rho_{\vec{Q}}(t) \rho_{\vec{Q}}^*(t) \rangle / N$  at wave vector  $\vec{Q}$  values, ranging from the smallest value  $2\pi/L$  allowed by the side  $L$  of the simulation box up to  $50 \text{ nm}^{-1}$ . The oxygen density fluctuation  $\rho_{\vec{Q}}(t) \equiv \sum_{i=1}^N \exp(i\vec{Q} \cdot \vec{r}_i)$ , where  $\vec{r}_i$  is the oxygen coordinate of molecule  $i$ . The onset of crystallization coincides with the occurrence of (i) a sudden drop in potential energy and (ii) a sharp increase in the density fluctuations at one or more wave vector values. When crystallization occurs, the value of  $S_{\vec{Q}}(t)$  jumps from  $\mathcal{O}(1)$  in the liquid to  $\mathcal{O}(N)$ .

Defining the crystallization time is somewhat arbitrary because of the stochasticity which accompanies the onset of crystallization and the definition of the critical nucleus. We define  $\tau_{cryst}$  as the time at which *any* density fluctuation  $S_{\vec{Q}}(t)$  grows above a threshold value  $S^* = 15$  and remains continuously above the threshold for a

time exceeding  $t^* = 40$  ps. This threshold prevents transient density fluctuations from being attributed to crystallization. We also perform calculations for other definitions of  $S^*$  and  $t^*$ , but the above values are sufficient to unambiguously identify the onset of crystallization without requiring excessive simulation time. Fig. 2.5 shows the crystallization times  $\tau_{cryst}$ , averaged over the four independent runs, for two different densities and for a broad range of  $T$ . The resulting TTT curve shows a characteristic “nose” shape, arising from the competition between two effects, the thermodynamic driving force for nucleation and the kinetics of growth [2, 29]. As temperature is lowered, both the thermodynamic driving force and the relaxation time increase, and it becomes more difficult for particles to diffuse to the energetically-preferred crystalline configuration. For both densities,  $\rho = 1.15$ , and  $1.20$  g/cm<sup>3</sup>, the  $T$  at which nucleation is fastest is around 240 K. At this  $T$ , the onset of crystallization requires about 3 ns. At the lowest studied  $T$ , the crystallization time has grown to 30 ns.

Fig. 2.5 also shows the relaxation times  $\tau_\alpha$ . The  $T$  dependence of  $\tau_\alpha$  can be described by a power law  $\tau_\alpha \propto (T - T_c)^\gamma$ , in agreement with the prediction of mode coupling theory [17]. Since the relation  $\tau_\alpha \ll \tau_{cryst}$  holds at each temperature, including in the deeply supercooled region, “equilibrium” studies of metastable water can be achieved before nucleation takes place. The supercooled liquid can be connected to the deeply supercooled glassy states via “equilibrium” metastable states if we choose a quench rate larger than the critical cooling rate  $\mathcal{R}_c \equiv (T_m - T_n)/\tau_n$ , where  $T_m$  is the melting  $T$  and  $T_n$  and  $\tau_n$  locate the nose in the TTT curve [2]. For TIP5P,  $\mathcal{R}_c \approx 10^{10}$  K/s at the two studied densities. For  $\rho = 1.10$  g/cm<sup>3</sup> and  $T = 240$  K, we observe only one (out of four) crystallization event within a time of 70 ns. For densities smaller than  $\rho = 1.10$  g/cm<sup>3</sup>, we observe no crystallization events within a time of 60 ns and hence we can only estimate that  $\mathcal{R}_c$  is smaller than  $10^9$  K/s (the experimental value for water at ambient pressure is  $\mathcal{R}_c \approx 10^7$  K/s [37]).

In Fig. 2.6 we show a typical crystal configuration. The crystal structure, after energy minimization at constant volume, is a proton-ordered structure similar to ice-B, first observed by Baez and Clancy[33]. Ice-B is a variant of the ice IX structure, which is the proton-ordered form of ice III. The density of ice IX and ice III is in fact  $1.16 \text{ g/cm}^3$ , close to our value.

## 2.5 Conclusion

We have shown that the liquid-liquid phase separation can be observed in metastable equilibrium (*i*) if the cooling rate is faster than  $\mathcal{R}_c$ , and (*ii*) if the observation time is shorter than the crystallization time at the critical point. While both such conditions can be realized in numerical simulations — as shown here — they cannot be met in experiments. Our simulations also show that a continuity of states between liquid and glassy phases of water exists [38]. Liquid states below the crystallization temperature can be accessed provided the cooling rate exceeds  $\mathcal{R}_c$ .