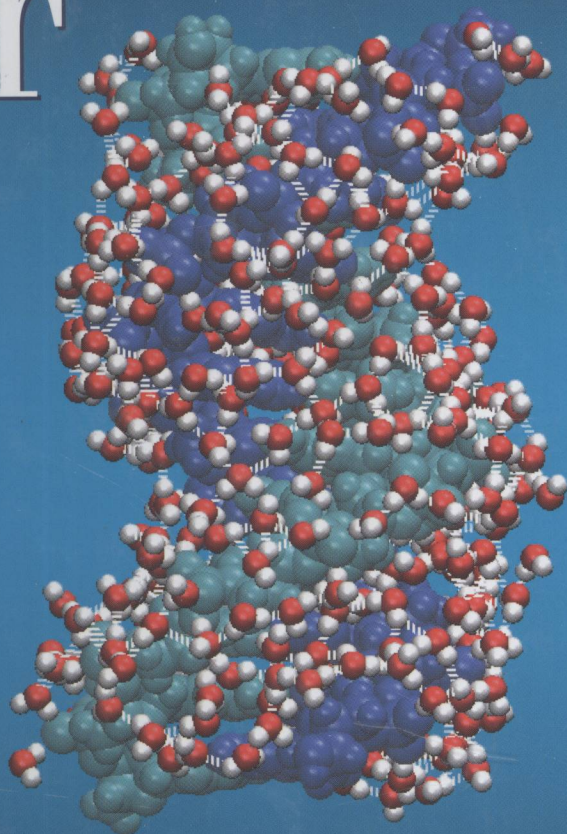# Interfacial
and
Confined
Water

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INTERFACIAL AND CONFINED WATER

BY

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Preface

Abundance of water on the earth and in space makes it involved in the processes that are interesting for researches in various fields of science and technology. For better understanding of these processes, it is necessary to characterize water properties in a wide range of thermodynamic conditions. Similar to other substances, water can exist in various phase states with essentially different properties: vapor, liquid, crystalline phases, amorphous phases, glassy states. Therefore, characterization of water properties should be based on the phase diagram, which shows location of the phase transitions in thermodynamic space, i.e. in temperature, pressure, density and other coordinates. Major part of water on the earth is the *bulk* phases: liquid phase in oceans, crystalline forms in polar ice caps and in glaciers, vapor phase in the air. Both on the earth and in space, essential amount of water is affected by the proximity of various boundaries. A bulk three-dimensional phase may be terminated by another phase of the same substance when two phases coexist. For example, a liquid and vapor being at coexistence form liquid–vapor interface. Besides, a boundary may be formed by another substance being in crystalline or amorphous phase, by extended surface of some macromolecular structure, etc.

The *interfacial* water, that is water near a boundary, plays an important role in various biological, geological, technological, and other processes. For example, life is not possible without water, which exists mainly as interfacial water in living organisms. The presence of boundary breaks the translational invariance present in a bulk system. As a consequence, all system properties become local, i.e. dependent on the position of the part of fluid considered relative to the boundary. The phase diagram of any substance including water becomes much more complicated near a boundary, in particular due to the appearance of the *surface transitions*. Besides, the critical behavior of a fluid is strongly modified

near a boundary, which strongly affects the fluid properties in a wide temperature range.

Finite extension in one or more spacial directions makes the system to be trapped in the pore geometry, which causes further complications of its phase behavior. The phase diagram of a system, confined between two planar boundaries or within cylindrical boundary, differs from the bulk one. In particular, bulk phase transitions and surface transitions are modified due to the confinement in pores. Structure of the real porous materials is often far from the simple slit or cylindrical geometry. Moreover, various porous media possess a highly disordered structure, and this disorder further complicates the phase behavior of a confined system. On the earth, *confined* water may be found in various geological materials, which possess a porous structure permeable for water. Considerable amount of water in living organisms is confined in cells and their counterparts. Confined water can be often found in porous materials used in technological processes. Essential amount of confined water may be expected in comets, which presumably represent a mixture of dust and ice.

To understand specific properties of interfacial and confined water at various thermodynamic conditions, we have to characterize the phase diagrams of water near surfaces and in various pores. A wide variety of such phase diagrams is expected, as they depend on the strength of the water–wall interaction, heterogeneity, roughness and curvature of a wall, pore size, and shape, etc. Knowledge of these phase diagrams opens a way for the description of the water *density distribution* near the surfaces and in pores, which is crucial for various structural and dynamic water properties. Subsequent analysis of the properties of interfacial and confined water allows understanding of related phenomena. Naturally, the phase behavior and properties of water show some regularities, which are universal for a wide class of fluids or even lattice systems. Knowledge of these universal features allows to distinguish them from the peculiar features, which are connected, first of all, with the strongly anisotropic hydrogen-bonding interactions between water molecules.

In Section 1 of this book, we give a brief description of the phase diagram of bulk water. This includes analysis of the liquid–vapor coexistence curve of water, a possibility to describe it in a universal way, effect of the liquid–vapor critical point on the properties of supercritical

water, etc. Besides, we consider some peculiar properties of a liquid bulk water, which appears at ambient and supercooled temperatures. The relation of these properties to the polyamorphism of water and to the liquid–liquid transitions of supercooled water is discussed. Surface phase diagram of water is described in Section 2. Analysis of the surface transitions of water starts with the brief overview of the theoretical, experimental, and simulation results obtained for lattices and simple fluids (Section 2.1). This is followed by the analysis of the surface transitions of water near hydrophilic (Section 2.2) and hydrophobic (Section 2.3) surfaces. Finally, the surface phase diagram of water is presented in Section 2.4. Section 3 is devoted to the surface critical behavior of water, which allows description of water density profiles near various surfaces. This analysis, presented in detail in Section 3.2, is based on the theory of the surface critical behavior and its implementation in simple fluids (Section 3.1). In Section 4, we consider the modifications of the phase diagram of water due to confinement in pores. A brief overview of the general theoretical expectations and the results for simple fluids is given in Section 4.1. Phase transitions of water in various pores are discussed in Section 4.2. Phenomena of capillary evaporation and capillary condensation and characteristic properties of water in pores are briefly described in Section 4.3. Upon adsorbing at hydrophilic surfaces, water may form mono- or bilayers (Section 5). In Section 5.1, we consider a percolation transition of water at hydrophilic surfaces, which results in the formation of water monolayer. Main structural properties of water layers at hydrophilic surfaces are described in Section 5.2. Role of interfacial water in biology is analyzed in Section 6. In this analysis, we show how various forms of biological activity depend on hydration level, temperature, and pressure. To clarify the role of interfacial water in biological function, we consider separately low-hydrated (Section 7) and fully hydrated (Section 8) biosystems. Experimental and simulation studies of the percolation transition of hydration water in biosystems are summarized in Section 7.1. The effect of this transition on various properties of biosystems is analyzed in Section 7.2. For fully hydrated biosystems (Section 8), we analyze the effect of temperature and pressure on the various properties of hydration water, including connectivity of the hydrogen bonds within the hydration shell. The effect of the state of hydration water on the properties of biosystems is discussed. Finally,

we summarize the current understanding of the properties of interfacial and confined water and formulate the open questions and controversial problems in Section 9.

In closing, we would like to express our deep gratitude to Alfons Geiger for his hospitality, fruitful collaboration, support of our initiatives in studies of water, and patience. We have greatly profited from collaboration with Roland Winter, Nikolay Smolin, Aljaksei Krukau, and Alexey Mazur. Our view on the properties of interfacial and confined water presented in this book is based on the fundamentals of the theory of phase transitions and critical phenomena in presence of a boundary, and we are greatly indebted to Kurt Binder, Michael Fisher, Gene Stanley, Robert Evans, Pablo Debenedetti, Gerhard Findenegg, and Josef Indekeu for elucidated and encouraging discussions, criticisms, and advices. This book has been made possible by financial support of our researches by Deutsche Forschungsgemeinschaft through the Forschergruppe 436 "Polymorphism, dynamics and functions of water near molecular boundaries," Schwerpunktprogramm 1155 "Molecular modeling and simulations in technology," and Graduiertenkolleg 298 "Structure-Dynamics Relations in Microstructured Systems," and by Bundesministerium fur Bildung und Forschung through the grant 01SF0303.

Contents

1   Phase diagram of bulk water

Properties of bulk fluid in distinct phase states differ so strongly that gas, liquid, and solid states are studied in different fields of statistical mechanics. Phase state of a system may be identified based on the phase diagram. Phase diagram of bulk water describes how the phase state of water changes with temperature and pressure. It includes the liquid–vapor, liquid–solid, and solid–solid phase transitions and also hypothesized transitions between amorphous (glassy or liquid) phases of supercooled water. In the solid state, water may form more than 14 crystalline forms [1]. Among these ices, the hexagonal ice is the most abundant. At atmospheric pressure, liquid water freezes into hexagonal ice at 273.15 K. This liquid–solid transition is accompanied by the decrease in water density by about 8%. Other ices can be obtained by increasing the pressure above 2 kbar. In particular, liquid water freezes into one of the high-density ices at ambient temperature when the pressure exceeds 6 kbar.

Major amount of water on the earth exists in the liquid bulk phase, which is close to the coexistence with a bulk water vapor present in the air. Therefore, the liquid–vapor phase transition is of special importance for understanding the water properties in the most of practically important situations. Bulk liquid water coexists with saturated vapor in a wide temperature range of about 374 K from the freezing temperature up to the liquid–vapor critical point. The liquid–vapor coexistence curve of bulk water, i.e. the temperature dependence of the densities of liquid (ρ_l) and vapor (ρ_v) coexisting phases, is shown in Fig. 1 by solid line. A stable bulk vapor phase exists at the densities left to the lower density branch of the coexistence curve. Accordingly, a stable bulk liquid phase exists at the densities right to the high-density branch of the coexistence curve. Water with a density inside two-phase region bounded by the coexistence curve is not thermodynamically stable, and it decomposes into two coexisting phases with the densities ρ_l and ρ_v. By increasing the temperature, two coexisting liquid and vapor phases become more and more similar in their properties until, at the critical point, all differences vanish. Beyond the critical point, only one homogeneous equilibrium water phase can exist, and all changes are continuous and smooth. The coexistence pressure near the melting point is about $6 \cdot 10^{-3}$ of ambient pressure (1 bar),

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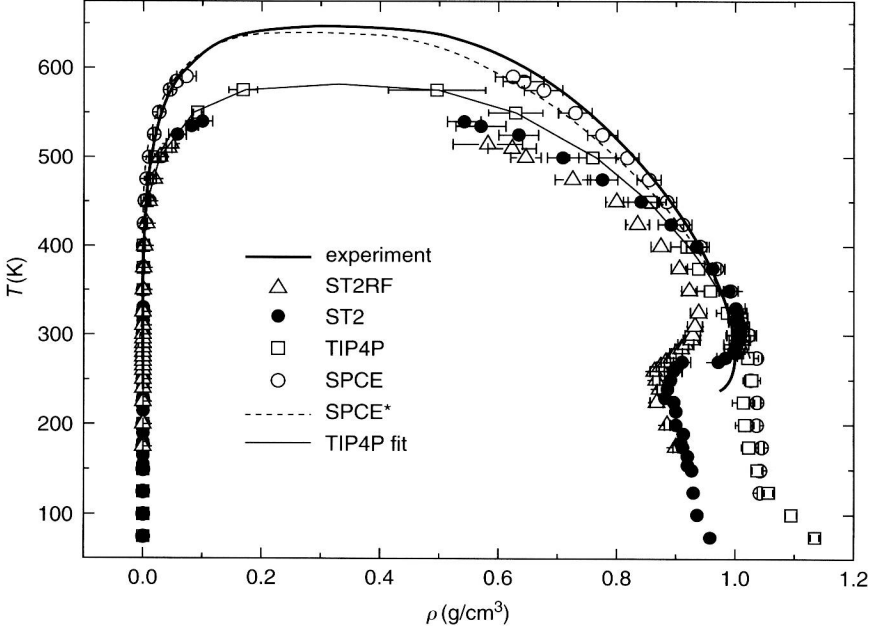
Figure 1: Experimental liquid–vapor coexistence curve of water [3] (thick solid line). Liquid–vapor coexistence curves of several water models: ST2 [6, 10], ST2RF [6], TIP 4P [6], SPCE [6], and SPCE* [11]. Fit of the data for the TIP 4P model to the extended scaling equation with leading asymptotic behavior described by eq. (1) is shown by thin solid line.

and it increases by a factor of $\sim$36 000 when approaching the critical point (Fig. 2). The liquid–vapor critical point of water is located at the critical temperature $T_c = 647.096$ K, critical pressure $P_c = 22.064$ MPa, and critical density $\rho_c = 0.322$ g/cm^3 [2, 3].

Although the liquid–vapor phase transition of bulk water is well studied experimentally, this is not the case for the phase transitions of interfacial and confined water, which we consider in the next sections. Therefore, studies of the phase transitions of confined water by computer simulation gain a special importance. For meaningful computer simulations, it is necessary to have water model, which is able to describe satisfactorily the liquid–vapor and other phase transitions of bulk water. The coexistence curves of some empirical water models, which represent a water molecule as a set of three to five interacting sites, are shown in Fig. 1. Some model adequately reproduces the location of the liquid–vapor critical point and,
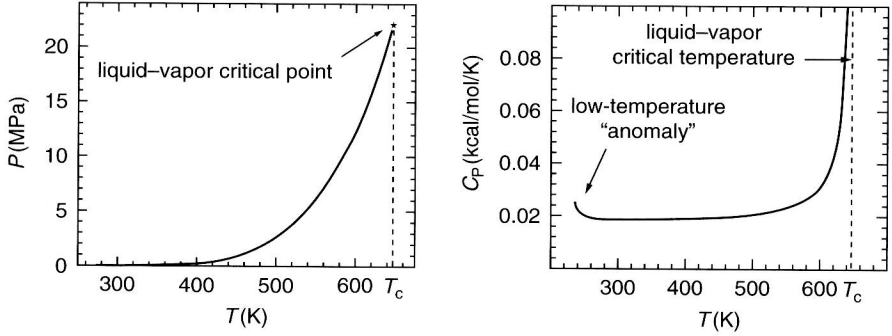
Figure 2: Left: liquid–vapor coexistence curve of water in the pressure–temperature plane from freezing temperature to the critical point [3]. Right: isobaric heat capacity C_P of liquid water along the liquid–vapor coexistence curve [3, 20].

accordingly, the temperature dependence of the liquid water density at high temperatures (SPCE model, see Fig. 1). However, the same model gives extremely low freezing temperature of water of about 214 K [4]. The comparative analysis of various water models can be found in Refs. [5–8]. Generally there is no empirical water model, which adequately describes the whole phase diagram of bulk water. This is not surprising as most of the popular water models were parameterized to fit some of the water properties at some particular thermodynamic conditions. Probably, the phase diagram of water in a wide thermodynamic range cannot be reproduced by a water model with just a few sites [9]. Therefore, there is an urgent need in more adequate water models. The available water models should be used with caution, keeping in mind their limited abilities to reproduce the phase diagram and properties of water quantitatively.

Upon heating, the densities of the coexisting vapor and liquid phases approach each other, and, asymptotically close to the critical temperature, their difference follows the universal power law:

$$\Delta\rho = (\rho_1 - \rho_v)/2 = B_0\tau^\beta, \tag{1}$$

where $\Delta\rho$ is the order parameter of phase transition, $\tau = (T_c - T)/T_c$ is a reduced deviation of temperature from T_c, $\beta \approx 0.326$ [12] is a universal critical exponent, and B_0 is a system-dependent amplitude. The behavior of $\Delta\rho(\tau)$ is shown in a double-logarithmic scale in Fig. 3, where power law (1) is shown by straight dashed lines. In the temperature

interval $\sim 130°$ below T_c ($\tau \leq 0.2$), $\Delta\rho(\tau)$ closely follows the asymptotic power law, whereas more complicate description is clearly necessary far away from T_c. In a wider temperature interval, order parameter may be described by the extended scaling equation using Wegner expansion [13]. The temperature dependence of the order parameter $\Delta\rho(\tau)$ of water may be described satisfactorily using several nonasymptotic corrections [11]:

$$\Delta\rho = 2.02\tau^{0.325}\left(1 + 0.396\tau^{0.5} - 1.35\tau + 1.63\tau^{1.5} - 0.693\tau^2 - 0.37\tau^{2.5}\right). \tag{2}$$

The diameter ρ_d of the coexistence curve is the average value of the densities of the coexisting liquid and vapor phases. It is equal to the critical density at $T = T_c$ and changes mainly regulary with τ. In the close vicinity of the critical point, diameter of fluids shows a critical anomaly, which may behave as $\sim \tau^{1-\alpha}$ [14] or $\sim \tau^{2\beta}$ [15], or as superposition of two contributions [16], where $\alpha \approx 0.11$ [12]. Diameter of the coexistence curve of bulk water may be described by the following equation [11]:

$$\begin{aligned}\rho_d &= (\rho_l + \rho_v)/2 \\ &= \rho_c\left(1 + 1.45\tau^{1-\alpha} - 0.10\tau - 0.35\tau^{1.5-\alpha} - 0.13\tau^{2-\alpha} - 1.35\tau^{5.5}\right).\end{aligned} \tag{3}$$

Universal behavior of the order parameter as well as of other thermodynamic properties near the critical point originates from the dominant role of the density fluctuations close to the T_c [17, 18]. When approaching the critical point, density fluctuations strongly increase and the correlation length ξ, which describes their growth (extension), diverges as $\xi = \xi_0\tau^{-\nu}$, where $\nu \approx 0.63$ [12] is a universal exponent and $\xi_0 \approx 0.694$ Å for water along the coexistence curve [19]. Under such circumstances, the microscopic details of system structure are not important, and thermodynamic properties depend mainly on the distance to the critical point expressed in terms of temperature, pressure, or density. The thermodynamic domain of universal behavior depends on the property considered, and it does not extend over more than several degrees for shear viscosity, for example. Strictly speaking, the true asymptotic range for the order parameter $\Delta\rho$ is also rather narrow. However, the corrections for nonasymptotic behavior notably compensate each other, providing the behavior close to eq. (1) in the temperature range of dozens and hundreds degrees. For instance,

the $\Delta\rho$ of model Lennard-Jones (LJ) fluids, which are used to describe such simple fluids as noble gases, shows behavior close to the $\sim \tau^\beta$ in the whole range of the existence of a liquid phase, i.e. from T_c to freezing temperature (see Fig. 3). This "critical-like" behavior of the order parameter in a wide temperature range is surprising because density fluctuations seem to be negligible far away from the critical point.

When approaching the critical point, all thermodynamic properties of systems behave in anomalous way [18, 21]. In particular, isothermal compressibility and heat capacity diverge, whereas diffusivity and other dynamic properties show a critical slowing down. An example of the critical divergence is shown in Fig. 2 for isobaric heat capacity C_P of liquid water along the coexistence curve. The critical anomalies of various properties are similar when approaching T_c along the coexistence curve or from supercritical temperatures along the critical isochore. At a given supercritical temperature, a property shows remnant of the critical anomaly, which is the largest at some pressure–density point. As a result, there are a number of specific lines in T–ρ plane in supercritical region, which emanate from the critical point and mark some specific
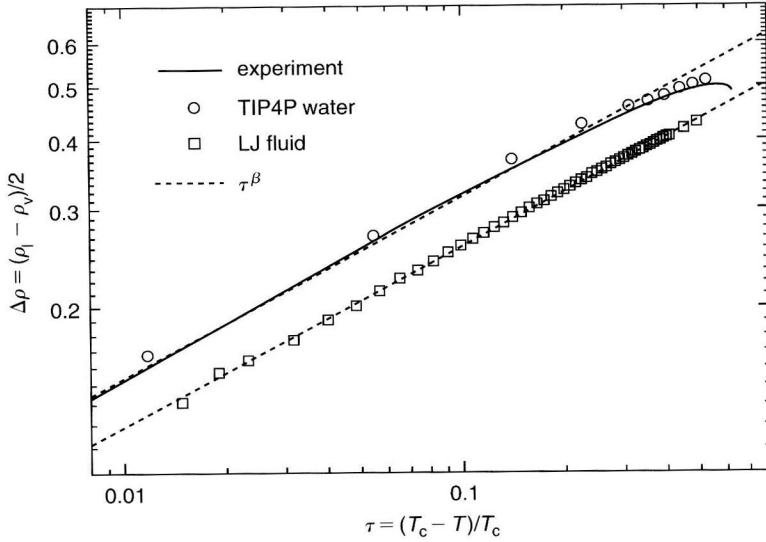
Figure 3: A log–log plot of the order parameter $\Delta\rho$ vs reduced temperature τ for real water [3] (thick solid line), TIP4P water model [28], and for LJ fluids [29]. Scaling equation (1) with $\beta = 0.326$ [12] is shown by straight dashed lines.

change in thermodynamic properties. In Fig. 4, we show the location of minimum of speed of sound [22] and approximate location of the maxima of isobaric and isochoric heat capacities [3]. There is one more important line emanating from the critical point, the line of percolation transitions of physical clusters [23]. This line separates two distinct states of supercritical water: there is an infinite hydrogen-bonded water network at higher density side, and only finite water clusters may be found at the lower density side. The percolation transition of supercritical model water, whose critical temperature is close to the one of real water [24, 25], is shown by a star. The expected line of the percolation transitions of water is shown schematically by thin solid line in Fig. 4. Obviously, more water density is required for the infinite network at higher temperatures, as hydrogen bonds break upon heating. Note that an infinite water network always exists in a liquid phase of water [26, 27]. At subcritical
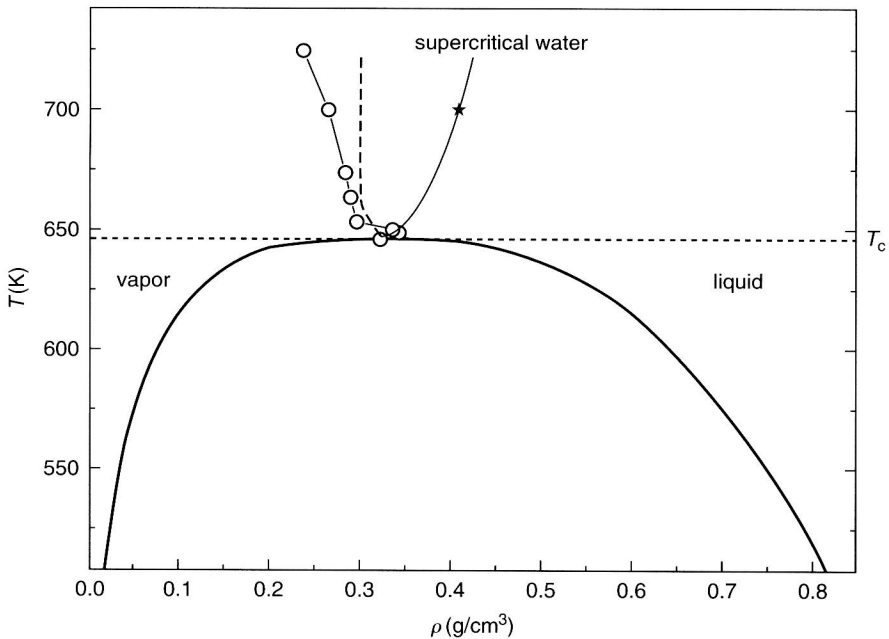
Figure 4: Liquid–vapor coexistence curve of water (thick solid line) and various specific lines emanating from the critical point: maximum heat capacity C_P [3] (dashed line), minimum speed of sound [22] (circles), and percolation transition of water clusters [24] (star).

temperatures, the break of an infinite water network in liquid water may be expected deeply inside the metastable region, i.e. at strongly negative pressures only.

Moving away from the liquid–vapor critical point, role of the density fluctuations diminishes, whereas the role of the molecular structure of fluids and local ordering of molecules become more and more important. Deviation from the asymptotic critical behavior of $\Delta\rho$ seen in Fig. 3 is a manifestation of this tendency. For water, deviations from the universal critical behavior start much closer to the critical point than for LJ fluid. This indicates stronger effect of fluid structure in the case of water. Moreover, due to this effect, the temperature dependence of the order parameter changes even qualitatively: below about 277.1 K (+4°C) [3], the densities of the liquid and vapor phases start to approach each other upon cooling due to the occurrence of the liquid density maximum. This is the most famous example of the specific properties of liquid water. Interestingly, this liquid density maximum is followed by a liquid density minimum in supercooled region. This means that at very low temperatures, liquid water behaves normally, i.e. it becomes more dense upon cooling. The density minimum of liquid water was first found in computer simulations of various water models [6, 30–34] (see Fig. 1) and later was observed in experiments with supercooled confined water [35]. Many other properties of liquid water also show specific behavior upon cooling (see [36–38] for reviews). For example, isobaric heat capacity shows rapid growth upon cooling (Fig. 2), which may be treated as a divergence at $T \approx 228$ K [39, 40]. Isothermal compressibility shows rather similar nonmonotonous temperature dependence [41, 42]. To understand the origin of these specific properties, we consider local ordering of molecules in liquid water at various temperatures.

The structure of condensed water phases is determined by the ability of water molecule to form four highly directional hydrogen bonds with the nearest neighbors. Accordingly, the tetrahedral arrangement of the four nearest neighbors is an important structural element of liquid water. In such arrangement, four nearest neighbors form almost perfect tetrahedron with a water molecule considered in its center. Tetrahedral ordering may be characterized by the tetrahedricity parameter [43], which measures deviation of the tetrahedron from ideal one and allows distinguishing of the tetrahedrally ordered water molecules [6, 10, 44, 45].