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Which Shape Characteristics of the Intermolecular Interaction of Liquid Water Determine Its Compressibility?

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We consider a fluid of spherical particles with a pair potential given by a hard core repulsion and a tail, and show that the isothermal compressibility of liquid water is determined by the degree of steepness of the soft repulsion near the hard-core contact. This helps us understand the thermodynamic mechanism that causes the compressibility anomaly of liquid water.

Keywords: isothermal compressibility, liquid water, intermolecular interaction, thermodynamic mechanism, Ornstein-Zernike approximation

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1. INTRODUCTION

It is well-known that the properties of liquid water at low temperatures change in much different ways than those exhibited by most other liquids under similar conditions [1]. These properties are determined by the interactions between water molecules, which can be derived by using thermodynamics and statistical mechanics. Therefore, it is important to study the relationship between the shape of the intermolecular interaction and each anomalous property of liquid water.

The development of realistic water models has recently shown great progress. Many of the experimentally observed anomalies of water have been reproduced in molecular dynamics or Monte Carlo simulations that use empirical force fields, albeit with significant differences in the predictions given by different models [2–11]. Among these, TIP4P/2005 probably gives the best agreement with experiment for a wide range of states and water properties [12–19]. However, no realistic models put forward up to now explains what characteristics of the intermolecular interactions determine the properties of liquid water. Realistic models can provide a description of the density and compressibility anomalies and reproduce a number of the other anomalies of water. However, the direct causes remain obscure and difficult to elucidate because such models include a number of properties of water, not all of which are related to the immediate causes. Therefore, it is impossible to capture the essential physics via the study of realistic models that include the miscellaneous properties of water, even if they can reproduce all of water's anomalies.

To capture the physics underlying a water anomaly, one should use simplified or core-softened models that include only the properties crucial to explaining that anomaly. It is important to address the mysteries individually, accumulate knowledge, and develop ideas. It is impossible to illuminate the direct causes of all the anomalies of water simultaneously. Toward this aim, a number of core-softened and simplified models have been put forward and used to perform numerical simulations. None of them [20–32]., however, has quantitatively reproduced any anomaly of liquid water or elucidated the thermodynamic mechanisms that cause the anomaly. The author believes that the self-consistent Ornstein-Zernike approximation (SCOZA) with hard-core repulsion plus Yukawa tails is presently the most useful. The SCOZA is known to describe the overall thermodynamics of liquids very well and provides a remarkably accurate critical point and coexistence curve. This scheme is entirely self-contained, which means that no supplementary thermodynamic or other input is necessary [33–40].

Recently, we have determined many functional representations of intermolecular interactions between water molecules that reproduce the experimentally measured density-temperature relation at 1 bar with a reasonable accuracy by using the SCOZA [39]. Numerous similar descriptions of pair interactions will be increasingly discovered in the coming years, which will help us to understand why solid water has polymorphic structures and liquid water has a large number of anomalies.

We have also elucidated the thermodynamic mechanisms that cause the density anomaly of liquid water [40]. Our model exhibits an unusual negative thermal expansion when the value of the potential tail at the hard-core contact is in some specific range, otherwise, the density anomaly does not occur in the system. The range depends on the shape of the attraction. The thermodynamic properties of liquid water can be derived from the excess internal energy. The negative thermal expansion of liquid water below 4°C is induced by the behavior of excess internal energy, which is mainly determined by the large positive value of the soft repulsive tail near the hard-core contact.

Russo and Tanaka [19] used a two-state model to describe the behavior of liquid water over a wide region of the phase diagram. The first state is denoted as the S state, in which local structures have low energy, high specific volume, and low degeneracy. In contrast, structures in the second state are thermally excited, characterized by a high degree of disorder and degeneracy, and have low specific volume and high energy. These structures are labeled as the ρ state. However, Russo and Tanaka [19] do not explain what causes the decomposition of water into the two states. We can explain the decomposition based on the thermodynamic mechanisms described in the above paragraph [40] as follows: Cooling of water generates the higher density ρ state structures and increases their excess internal energies because of the high values of the soft-repulsive potential near the hard-core contact due to condensation. This causes the derivative α of the pressure with respect to temperature at constant density to be negative, resulting in negative thermal expansion, which generates the S state structures. In this way, we can understand that the decomposition of water into the two states is not the cause of the anomaly but just an accompanying effect. Furthermore, no idea put forward up to now tells us anything about what induces negative thermal expansion. However, we can explain the cause in the same way. Cooling of water may generate denser proper water complexes [41], a denser quartz-like structure [42], hydrogen bond bending [43], or the filling of cavities [44, 45]. Their excess internal energies become higher because of the high values of the soft-repulsive potential near the hard-core contact due to condensation. The coefficient α becomes negative, resulting in negative thermal expansion, which may generate less dense and ice-like complexes [41], less dense tridymite-like ones [42], stretching of the hydrogen bond bending [43], or preventing the cavities from filling and causing negative expansion [44, 45].

It is well-known that almost none of the ideas put forward [41–54] explain what causes the negative thermal expansion at temperatures below 4°C. For example, one claim is that the tetrahedral structure of ice causes the density anomaly, but there is no evidence for this. As a counter analogy, consider a folding umbrella. To open or close it, one pushes or pulls the base of the frame with hand power. The frame has no power to open or close itself without human intervention. In the case of the umbrella, the direct cause of its expansion and contraction is human hand power and not the frame itself. To clarify the thermodynamic mechanism that causes the density anomaly, it is necessary to find what acts as an attractive force to condense water at temperatures above 4°C, but acts as a repulsive force to expand water below 4°C with reducing temperature. Such a force (hereafter referred to for simplicity as the "anomaly force") is the immediate cause of the density anomaly of liquid water. It is difficult to imagine how the tetrahedral structure could create an "anomaly force"analogous to the case of the folding umbrella.

Another suggestion is that hydrogen bonding causes the density anomaly. However, hydrogen bonding is attractive at any temperature and has the tendency to reduce the distance between molecules in thermodynamic equilibrium to condense liquid water. Therefore, it is difficult to consider how hydrogen bonding could turn into a repulsive force below 4°C and cause negative thermal expansion.

Regarding the network or clathrate models [10, 20–23], even though it may be plausible that isolated water molecules go into cavities as the temperature lowers to cause liquid water to condense, the models do not explain what makes isolated water molecules leave the filled cavities at temperatures below 4°C with reducing temperature and induce negative expansion.

Lactic acid was long believed to be the substance that causes muscle fatigue because it increases with fatigue, but lactic acid was recently found to be a substance that assists in recovery from fatigue. It is now known that active oxygen is the substance responsible for fatigue. Similarly, it cannot be claimed that the density anomaly is caused by some phenomenon just because it accompanies the density anomaly. We can apply this principle to almost every idea put forward until now.

Here, we present the idea that the thermodynamic mechanism found by Yasutomi [40] induces negative thermal expansion. This is accompanied by rearranging orientations of molecules and results in polymorphic structures of solid water depending on the shape of the orientation-dependent potential, or is accompanied by a second critical point, two-state structures, or clathrate structures. In this way, although our study is blind to freezing and, more generally, to the solid phases of the system, it presents significant insights into the thermodynamic properties of water in these phases. We expet that our main remarks may be applicable to a density anomaly in any liquid [39, 40].

We believe that mysteries in thermodynamic phenomena in nature are solved when the intermolecular interactions and the thermodynamic mechanisms that induce the phenomena are elucidated. From this point of view, we show in the present paper that the isothermal compressibility of liquid water is determined by the degree of steepness of the soft-repulsion near the hard-core contact. This helps us to understand the thermodynamic mechanism that causes the compressibility anomaly of liquid water.

2. MODELS AND NUMERICAL RESULTS

We consider a fluid of spherical particles with a pair potential given by a hard-core (HC) repulsion and some tail $\phi(r)$ that is expressed as

$$\phi(r) = \begin{cases} \infty & r < 1 \\ -\sum_{n=2}^{N} a_n \dfrac{\exp[-z_n(r-1)]}{r} & r \geq 1 \end{cases} \quad (1)$$

where N is an arbitrary integer and z_n and a_n are arbitrary constants. We consider three cases of tails $\phi_i(r)$ $(i = 1 - 3)$ and refer to the model with tail ϕ_i as "Model ϕ_i." The parameters a_n are listed in **Table 1**. The parameters z_n are given by $0.6395(n-1)$, $1.18(n-1)$, and $0.6[1+8(n-2)]$ for ϕ_1, ϕ_2 and ϕ_3, respectively. **Figure 1** shows these potential tails. The diameter σ_u of the hard core and the depth ε_u of the potential are used as units of length and energy, respectively, and are shown in **Table 2**.

We obtain the thermodynamic properties of the models by using the SCOZA [33–40]. We express the physical quantities by the same symbols, and the numerical computations are performed as described in Yasutomi [39, 40]. **Table 2** shows the density grid $\Delta\rho$, the temperature grid $\Delta\beta$, the density ρ_0 at which we made use of the so-called high-temperature approximation [55] and β_f. Nnumerical computations are performed in the range of $0 < \beta < \beta_f$.

TABLE 1 | Parameters a_n for ϕ_1, ϕ_2, and ϕ_3.

n	ϕ_1 a_n	ϕ_2 a_n	ϕ_3 a_n
2	+39.5839	+73.1654	+1.86973
3	−433.906	−320.979	−53.9562
4	+1478.56	−7597.99	+415.834
5	−1906.08	+64001.9	−1189.08
6	+791.644	−134345	+1456.07
7			−652.705

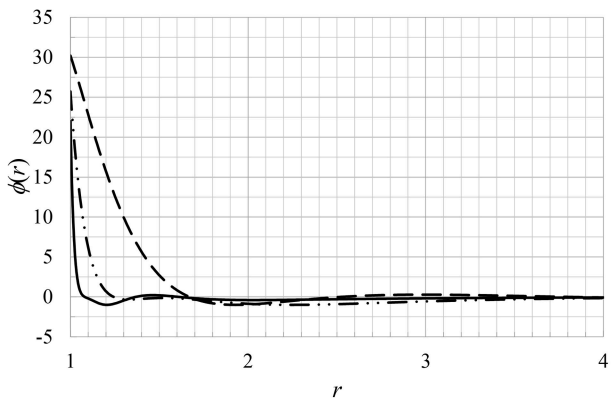

FIGURE 1 | Potential tails. Dashed, chain double-dashed, and solid lines exhibit ϕ_1, ϕ_2, and ϕ_3, respectively.

All three of the Models ϕ_1-ϕ_3 reproduce reasonably well the experimentally measured density-temperature relationship of liquid water at 1 bar as shown in **Figure 2**. The isothermal compressibilities are shown as a function of temperature at 1 bar in **Figure 3**. The plot demonstrates that the isothermal

TABLE 2 | Parameters used in numerical computations for Models $\phi_1 - \phi_3$.

	ϕ_1	ϕ_2	ϕ_3
$\Delta\rho$	0.001	0.001	0.0005
$\Delta\beta$	$2\times10^{-10} - 10^{-3}$	$10^{-5} - 2\times10^{-4}$	$10^{-7} - 10^{-4}$
ρ_0	0.748	0.827	1.0175
β_f	0.310	0.244	0.332
β_c	0.108	0.103	0.145
ρ_c	0.084	0.158	0.2165
ε_u(K)	74.65	59.92	78.97
σ_u(Å)	1.965	2.156	2.402

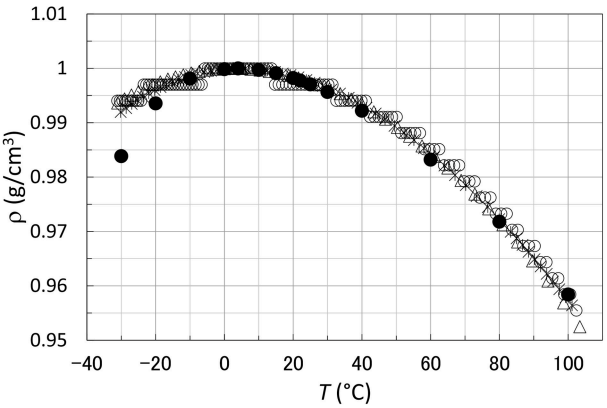

FIGURE 2 | Density-temperature relation of liquid water at 1 bar. Asterisks, triangles, open, and closed circles show those for $\phi_1(r)$, $\phi_2(r)$, $\phi_3(r)$, and experimentally measured data, respectively.

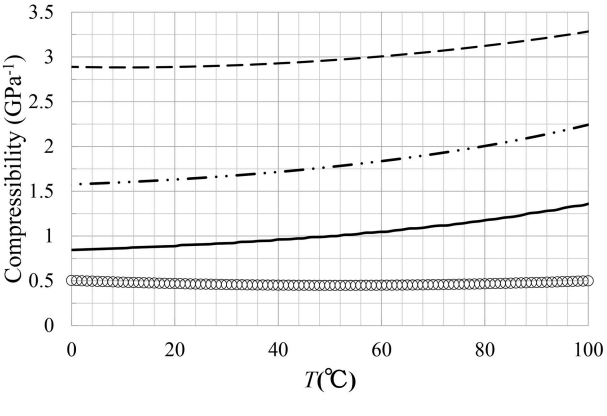

FIGURE 3 | Isothermal compressibility-temperature relation of liquid water at 1 bar. Dashed, chain double-dashed, solid lines, and open circles show those for $\phi_1(r)$, $\phi_2(r)$, $\phi_3(r)$, and experimentally measured data, respectively.

compressibility reduces with increasing degree of steepness of the potential tail near the hard-core contact.

3. DISCUSSION

Thermodynamic quantities can be derived from the excess internal energy u per unit volume defined by

$$u = 2\pi\rho^2 \int_1^\infty dr\, r^2 \phi(r) g(r)$$

where $g(r)$ is a distribution function. The excess internal energy is useful for studying the relationships between the shape of the intermolecular potential and the behavior of a thermodynamic quantity. We have illuminated the thermodynamic mechanism which causes the density anomaly of water through the excess internal energy in our previous paper [40].

The integrand in the above equation shows that the excess internal energy is given by the product of intermolecular interaction $\phi(r)$ and distribution function $g(r)$. This suggests that there are an infinite number of combinations of $\phi(r)$ and $g(r)$ that result in the same u, and we have determined many potential tails that reproduce the experimentally measured density anomaly of water at 1 bar in our recent paper [39].

Besides those, we also determined three pair interactions between water molecules (**Figure 1**), all of which reproduce the experimentally measured density anomaly at 1 bar with reasonable accuracy (**Figure 2**). **Figures 2**, **3** show that the degree of steepness of the tail near the hard-core contact determines the isothermal compressibility of a liquid. Among the models, Model ϕ_3 best reproduces the experimental data for liquid water. Therefore, tails steeper than ϕ_3 will likely reproduce the experimental data with even better accuracy. It will take much more calculation time to determine the functional representations of such potential tails because the steeper tails should be expressed with a smaller radial distance grid. In addition. numerical computations should be performed with smaller density and temperature grids to attain a more optimal accuracy. Nevertheless, in the comming years we should increasingly be able to discover potential tails that will reproduce the experimental data of both the density-temperature and compressibility-temperature relations at 1 bar with reasonable accuracy. These potential tails will help us to illuminate the physics underlying the numerous anomalies of liquid water. Our main remarks may be applicable to a density anomaly and a thermal compressibility in any liquid [39, 40].

AUTHOR CONTRIBUTIONS

The author confirms being the sole contributor of this work and approved it for publication.

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