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Why thermodynamic properties of normal and heavy water are similar to those of argon-like liquids?

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ABSTRACT

The Letter is devoted to the explanation of the argon-like behavior of the thermodynamic properties of water. It is shown that this phenomenon is caused by the averaged inter-particle potentials which form due to rotation of water molecules. The general structure of the averaged potentials is proposed. The physical nature for the considerable shift of the triple point of water in comparison with the one obtained by extrapolation in the homological series is discussed.

1. Introduction

Surprising properties of water in its liquid state are well known [1,2]. Among them, the special attention is usually paid to the non-monotonous temperature dependence of density, the large values of the dielectric permittivity and the local structure close to that in hexagonal ice. These as well as other surprising properties are connected with the existence of H-bonds in water.

The thermodynamic properties of water have been analyzed in Refs. [3–5] in the manner of the principle of corresponding states. In such a way the new type of the surprising properties was established: the temperature dependences of the specific volume per molecule and the heat of evaporation on the coexistence curve of water have the argon-like behavior. From the physical point of view such a similarity of thermodynamic properties is possible only in the case when the inter-particle potentials in water and noble gases have close structure. This circumstance is not easily accessible since in water the very important role belongs to H-bonds. However, the situation radically changes if we assume that the equation of state for water and, in particular, the behavior of the specific volume and the heat of evaporation is determined by the averaged inter-particle potentials. The natural cause for such averaging is the rotational motion of water molecules. The important information about the character of the rotational motion can be obtained from the study of the kinematic shear viscosity for water and argon.

In this work we investigate in detail the character of the averaged inter-particle potential in water. Since the character of the rotational motion of molecules in normal and heavy water is noticeably different, Section 2 is devoted to the comparative study of their thermodynamic properties on their coexistence curves. The structure and the parameters of the averaged intermolecular potentials are investigated In Section 3. Section 4 is devoted to the determination of the triple point of water, which position is very surprising with respect to the predictable locus in the series of water homologues. In Section 5 we consider the manifestation of H-bonds within our approach.

2. Experimental evidences for the similarity of thermodynamic properties of water and argon

In this section we (i) present weighty arguments which confirm that many thermodynamic quantities of water have argon-like behavior, and (ii) consider the distinctions in the behavior of the normal and heavy water, in which the rotation of molecules is noticeably different. The specific volume per molecule is the simplest and the most important of them. For our purpose, let us compare the temperature dependences of the specific volumes $v^{(i)}$ for water and argon ($i = \mathrm{H_2O}$, Ar) in the manner of the principle of corresponding states [6]. It implies that the ratio $R_v^{(\mathrm{H_2O})}(t) = \tilde{v}^{(\mathrm{H_2O})}(t)/\tilde{v}^{(\mathrm{Ar})}(t)$ of the reduced quantities $\tilde{v}^{(i)}(t) = v^{(i)}(t)/v_c^{(i)}$, where $v_c^{(i)}$ is the critical value of $v^{(i)}(t)$, should be presented as a

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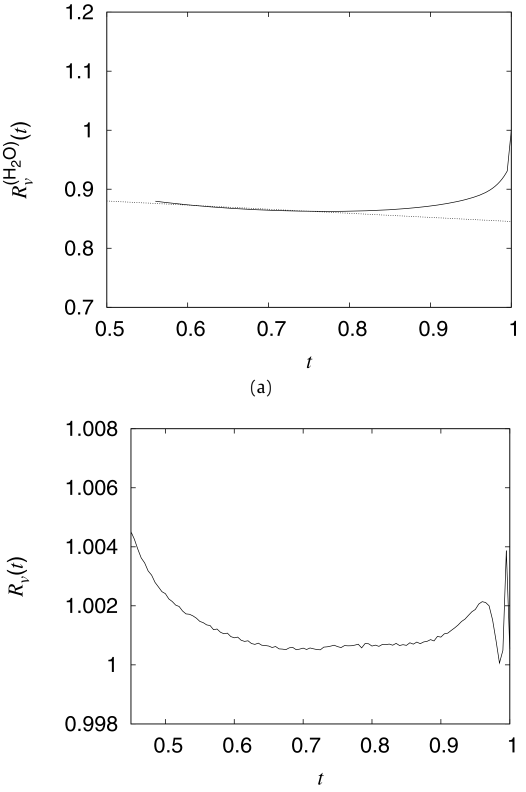


(a)

(b)

Fig. 1. The temperature dependence of the ratios (a) $R_v^{(\mathrm{H_2O})}(t) = \tilde{v}^{(\mathrm{H_2O})}(t)/\tilde{v}^{(\mathrm{Ar})}(t)$ and (b) $R_v(t) = v^{(\mathrm{D_2O})}(t)/v^{(\mathrm{H_2O})}(t)$ on the coexistence curves of the normal and heavy water according to Refs. [7,8].

function of the dimensionless temperature $t = T/T_c^{(i)}$, where $T_c^{(i)}$ is the critical temperature of the ith liquid. As seen from Fig. 1a, the temperature dependence of the specific volume for water is similar to that for argon practically in the whole temperature range of liquid states ($0.42 < t < 0.9$).

The ratio $R_v^{(\mathrm{H_2O})}(t)$ is with good accuracy approximated by the linear polynomial in the temperature interval $0.55 < t < 0.8$:

$$R_v^{(\mathrm{H_2O})}(t) = r_0^{(v)} + 4r_H^{(v)}(1 - \lambda_v t). \tag{1}$$

The coefficients r_0, r_H and λ, determined by fitting experimental data with the help of the least square method, are equal to:

$$\mathrm{H_2O}: \quad r_0^{(v)} = 0.827, \qquad r_H^{(v)} = 0.021, \qquad \lambda_v = 0.83; \tag{2}$$

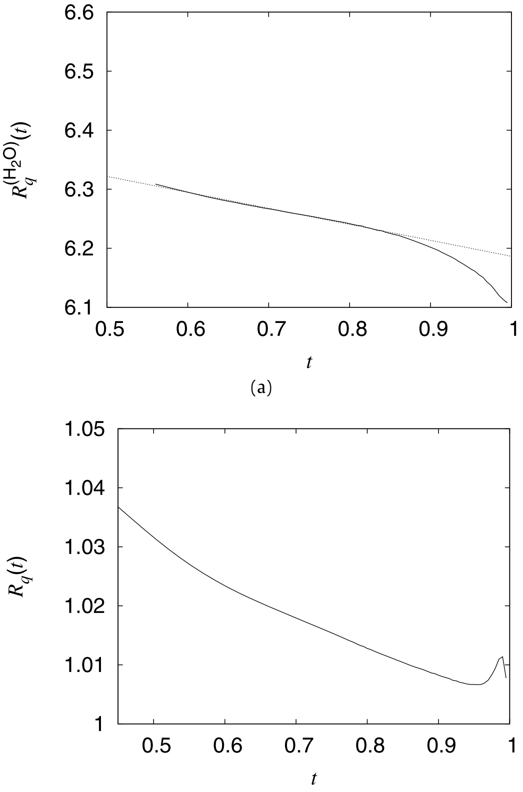
$$\mathrm{D_2O}: \quad r_0^{(v)} = 0.851, \qquad r_H^{(v)} = 0.021, \qquad \lambda_v = 0.83. \tag{3}$$

It was shown in Refs. [2,9] that the combination

$$n_H(t) = 4(1 - \lambda_v t) \tag{4}$$

has meaning of the average number of H-bonds per molecule. Thus, (i) the contribution of H-bonds to the specific volume per molecule does not exceed several percents, and (ii) the values of $n_H(t)$ for both normal and heavy water on their coexistence curves are practically the same. The deviation of $R_v(t) = v^{(\mathrm{D_2O})}(t)/v^{(\mathrm{H_2O})}(t)$ from unity for $t < 0.55$ indicates that the properties of the D-bond network insignificantly differ from those for the H-bond network only near the crystallization point and probably in the supercooled region.

The comparison of the heat of evaporation for water and argon is even more intriguing. The deviation of $R_q^{(\mathrm{H_2O})}(t)$ from the approximate value ≈ 6.2 does not exceed 1.1% (see Fig. 2a).



(a)

(b)

Fig. 2. The temperature dependence of the ratios (a) $R_q^{(\mathrm{H_2O})}(t) = q^{(\mathrm{H_2O})}(t)/q^{(\mathrm{Ar})}(t)$ and (b) $R_q(t) = q^{(\mathrm{D_2O})}(t)/q^{(\mathrm{H_2O})}(t)$ according to the experimental data [7,8].

As for the specific volume, the temperature dependence of the ratio $R_q^{(\mathrm{H_2O})}(t)$ is quasi-linear in the temperature interval $0.55 < t < 0.8$:

$$R_q^{(\mathrm{H_2O})}(t) = r_0^{(q)} + 4r_H^{(q)}(1 - \lambda_q t), \tag{5}$$

where

$$\mathrm{H_2O}: \quad r_0^{(q)} = 6.137, \qquad r_H^{(q)} = 0.080, \qquad \lambda_q = 0.85; \tag{6}$$

$$\mathrm{D_2O}: \quad r_0^{(q)} = 6.084, \qquad r_H^{(q)} = 0.182, \qquad \lambda_q = 0.85. \tag{7}$$

As we see, the values of $n_H(t)$ for the normal and heavy water determined from the temperature dependences of the heat of evaporation coincide with those determined from the specific volume per molecule within the experimental error. At the same time, the systematic increase of $R_q(t) - 1$ with lowering temperature reflects the behavior of the entropy. This effect deserves separate consideration.

The argon-like behavior of the ratios $R_v^{(i)}(t)$ and $R_q^{(i)}(t)$, $i = \mathrm{H_2O}$, $\mathrm{D_2O}$, is violated only in the narrow vicinity of the critical point: $0.85 < t < 1$. As shown in Ref. [10], it is connected with the dimerization of water molecules in the fluctuation region, where the doubled volume per molecule becomes greater than the volume occupied by a dimer.

Slight deviations of $R_v^{(i)}(t)$ and $R_q^{(i)}(t)$ from constant values are connected with the weak influence of H-bonds. This effect has the natural explanation: the behavior of the specific volume and the heat of evaporation for water is caused by the averaged intermolecular potentials. In turn, such an averaging is generated by the rotation of molecules. Due to this the H-bond anisotropic effects are practically lost.

The weak influence of H-bond effects is also manifested near the crystallization point. They lead to (i) the appearance of the