An Explanation of the Density Maximum in Water

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An explanation of the anomalous density maximum in water near 4 °C can be given in terms of a competition between the presence of open second-neighbor oxygen-oxygen structure at 4.5 Å and a dense second-neighbor structure obtained from the bending of hydrogen bonds. Since no computational model of water has provided an explanation of this anomaly, altering the water-water potential to create more realistic interactions in the second-neighbor shell is proposed. Support for this idea is provided here by considering the exactly soluble Takahashi fluid model.

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Liquid water is one of the most mysterious materials known. It is “a still poorly known liquid” [1]; an “anomalous liquid and solvent” [2]; and “we know how to work out the properties of ice and steam, but we have no clear idea why there is such a thing as ordinary liquid water” [3].

One of the most familiar mysteries is the density anomaly: At sufficiently low temperatures, warming the liquid causes it to *shrink.* There is an increasing awareness that understanding this one property will reveal the origins of all the other anomalous properties of water, and thus will provide a complete molecular-level description of this most important liquid. However, currently popular computational models of water are simply unable to reproduce this anomaly, as so aptly stressed in the abstracts of two very recent papers [4,5]. It would seem that, if a model does not possess this basic property of the real liquid, it cannot provide any sort of an accurate picture in biological, chemical, or geophysical applications, on which an ever increasing amount of computational effort is now being spent.

Recent experimental investigations have suggested important avenues of approach towards the ultimate resolution of this problem. For example, vibrational Raman data [6] over a range of temperatures from the supercooled region indicate a mixture of resonances, one exhibiting strong hydrogen bonding as in normal ice, the other having a lower degree of such bonding. Still more revealing are isochoric differential x-ray scattering data for liquid D_2O [7], again spanning both supercooled and normal temperature ranges. These results show the presence of at least two *second-neighbor* peaks in the radial distribution function, one near 3.4 Å, which grows in with increasing temperature differential, the other near 4.5 Å, which decreases with temperature. Apparently, as the temperature increases, more densely packed second neighbors near 3.4 Å are created in the liquid at the expense of the ordinary second neighbors of the open tetrahedral network. These new neighbors have already been described as “fifth neighbors” in the work of Sciortino, Geiger, and Stanley [8]. What further identification is possible?

From the early crystallographic work [9,10] it is already well know that changes in the crystal structures of the various ice polymorphs always occur *outside* the first-neighbor shell. Going to the second shell in normal ice Ih, the oxygen-oxygen distance is the continuation of the open tetrahedral network structure at ~4.5 Å. However, in the higher density ($\rho > 1.15$ g/cm^3) crystalline ice polymorphs, hydrogen bonds that form the second-neighbor shell are bent [9], creating condensed oxygen-oxygen distances. In fact, in the most stable moderately dense forms of ice, this second-neighbor distance lies near 3.4 Å. In a recent paper on neutron diffraction studies [11] of liquid D_2O under pressure down to temperatures of −65 °C, bond bending is again suggested: “The effect of pressure is subtle in the sense that it does not change substantially the number of hydrogen bonds, but the $\mathrm{O} \cdots \mathrm{O} \cdots \mathrm{O}$ angles are modified.” This is exactly what happens when the open oxygen-oxygen bonding in the second-neighbor shell changes over to the more dense structure at 3.4 Å. All these structural features in the liquid and in the crystalline polymorphs of water provide a picture that is in perfect concordance with the differential x-ray diffraction results [7] for the liquid, and help to identify the new neighbors as a structure already inherent in condensed phases of water. It seems clear then that the water-water potential in computational models should be modified in such a way that it can provide a subsidiary second-neighbor oxygen-oxygen minimum near 3.4 Å, while keeping intact under appropriate thermodynamic conditions the open tetrahedral structure.

In this Letter, the feasibility of the above idea is tested with an exactly solvable analytical model. In order to carry out this analysis, we must consider *only* second neighbors in liquid water, ignoring the first neighbors altogether. The justification for this simplification rests on two experimental properties, (1) the number density and structure in the first shell of the liquid are not strongly affected by temperature [7], and (2) the oxygen-oxygen nearest-neighbor distances in *all* forms of the liquid and ice are the same, ~2.8 Å [7,9,10]. For these reasons, nearest neighbors cannot play a significant role in

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determining thermally induced or pressure induced density variations in liquid water, except weakly through ordinary compressibility and thermal expansion. The nearest neighbors can be considered as part of an invariant inner "core." One might then expect that *the second-neighbor structure determines the density.* This structure is seen to depend on two minima, a close-in metastable one near 3.4 Å and a farther-out deeper minimum at ~4.5 Å. The shallower minimum may not be evident from quantum calculations on small water clusters, particularly the dimer.

Because of the foregoing considerations, an exactly solvable one-dimensional model can be employed for the investigation of the density maximum in water. We can simply treat the second neighbors in the real liquid as "first neighbors" in the theoretical model.

This type of problem was first solved for a hard sphere potential by Tonks [12], and was later generalized by Takahashi [13] and others [14]. The Hamiltonian in the Takahashi model is

$$\mathcal{H} = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \mathcal{V}(q_i), \tag{1}$$

where N particles each of mass m and momenta p_i have the potential energy

$$\mathcal{V}(q_i) = \sum_{i=1}^{N-1} v(|q_{i+1} - q_i|). \tag{2}$$

Since the system is to be studied for a range of temperatures and pressures, it is convenient to work in the isobaric-isothermal ensemble in which the partition function [15] is

$$Q_N(P,T) = \frac{1}{N!h^N} \int_0^\infty dL \int e^{-\beta(PL+\mathcal{H})}\, d^N q d^N p, \tag{3}$$

where L is the "volume" in the one-dimensional system, P is the "pressure," which is actually just the tension at the two ends of the fluid, and the other symbols have their usual meanings. The single integral sign collectively stands for N momentum integrals, with limits $-\infty$ to $+\infty$, and N position intervals, 0 to L. The Gibbs free energy is

$$G(P,T) = -k_B T \ln Q_N(P,T). \tag{4}$$

The momentum integrals in (3) may be evaluated to yield

$$\begin{aligned} Q_N(L,T) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{N/2} &\int_0^\infty dL e^{-\beta PL} \\ \times &\int_0^L dq_N \cdots \int_0^L dq_i \cdots \int_0^L dq_1 \\ \times &\exp\left[-\beta \sum_{i=1}^{N-1} v(|q_{i+1} - q_i|)\right]. \end{aligned} \tag{5}$$

The multidimensional *configurational* integral over the positions of all the particles can be determined exactly in one dimension by showing that it is $N!$ times the integral over the special region, $0 < q_1 < q_2 < q_3 \cdots < q_N < L$ [11–13]. Therefore the isobaric-isothermal partition function reduces to

$$\begin{aligned} Q_N(P,T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{N/2} &\int_0^\infty dL e^{-\beta PL} \\ \times &\int_0^L dq_N \int_0^{q_N} dq_{N-1} e^{-\beta v(q_N - q_{N-1})} \\ &\cdots \int_0^{q_2} dq_1 e^{-\beta v(q_2 - q_1)}. \end{aligned} \tag{6}$$

This integral is the Laplace transform of convolutions, so, using the convolution theorem [16], one obtains

$$Q_N(P,T) = \left(\frac{2\pi m k_B T}{h^2}\right)^{N/2} \frac{1}{\beta P} [\kappa(P,T)]^{N-1} \frac{1}{\beta P}, \tag{7}$$

where $\kappa(P,T)$ is the Laplace transform of $e^{-\beta v}$,

$$\kappa(P,T) = \int_0^\infty dx\, e^{-\beta P x} e^{-\beta v(x)}. \tag{8}$$

Now taking the thermodynamic limit in which $L \to \infty, N \to \infty$, while the volume per particle $l = L/N$ held constant, gives for the Gibbs free energy

$$G(P,T) = -\frac{N}{\beta}\left[\frac{1}{2}\ln\left(\frac{2\pi m k_B T}{h^2}\right) + \ln\kappa(P,T)\right]. \tag{9}$$

The total volume of the system in this limit is [17]

$$L = \left(\frac{\partial G}{\partial P}\right)_T = -\frac{N}{\beta\kappa(P,T)}\left(\frac{\partial\kappa(P,T)}{\partial P}\right)_T, \tag{10}$$

and the volume per particle l and the density ρ are given by

$$l = \frac{1}{\rho} = -\frac{1}{\beta\kappa(P,T)}\left(\frac{\partial\kappa(P,T)}{\partial P}\right)_T. \tag{11}$$

Therefore, to obtain the density, one must first choose a potential, then perform the κ integral in Eq. (8), and differentiate the result with respect to P.

In the original Takahashi model [13,14] there is a hard core for $0 < x < a$, and the potential is zero for $x > 2a$. Any analytically tractable potential can be used in the region $a < x < 2a$. In order to reproduce the second-neighbor characteristics of real water, we can therefore extend the Takahashi model to two wells, dividing the region between a and $2a$ into three equal parts. These parts correspond to an inner well, a plateau, and an outer well, respectively. The potential can then be written

$$v(x) = \begin{cases} \infty, & 0 < x < a; \quad \text{hard core,} \\ -\epsilon, & a < x < 4a/3; \quad \text{inner well,} \\ 0, & 4a/3 < x < 5a/3; \quad \text{plateau,} \\ -\lambda\epsilon, & 5a/3 < x < 2a; \quad \text{outer well,} \\ 0, & x > 2a, \end{cases} \tag{12}$$

remembering that the two second-neighbor wells in real water have been replaced here by nearest-neighbor wells. The quantities λ and ϵ are positive. The integral for κ yields

$$\kappa(P,T) = \frac{1}{\beta P}\,\theta^3[\phi + \theta(1-\phi) - \theta^2(1-\theta)(1-\phi^\lambda)], \tag{13}$$

where $\theta = e^{-\beta Pa/3}$ and $\phi = e^{\beta\epsilon}$. Using Eq. (11), the equation of state becomes

$$P(l-a) = k_BT + \frac{Pa}{3}\,\frac{\theta[1-\phi-\theta(2-3\theta)(1-\phi)^\lambda]}{\phi+\theta(1-\phi)-\theta^2(1-\theta)(1-\phi^\lambda)}. \tag{14}$$

It is easy to see that this equation reduces to the expected result in all appropriate limits—hard sphere, single well, ideal gas, etc.

Near absolute zero, θ is small and ϕ is large. The equation of state then reduces to

$$P(l-a) \approx k_BT + \frac{2Pa}{3}\,\frac{\theta^2\phi^{\lambda-1}}{1+\theta^2\phi^{\lambda-1}}. \tag{15}$$

In the case where the inner well is *deeper* than the outer well, $\lambda \le 1$ and terms involving ϕ vanish. Thus the right hand side of Eq. (15) goes to zero as $T \rightarrow 0$, and the crystalline state of minimum volume, $l = a$, where all the spheres are touching, is obtained. On raising the temperature, the system simply expands and no density maximum occurs.

On the other hand, for the case of "water," where the outer well is deeper ($\lambda > 1$), the terms involving ϕ are dominant, and at $T = 0$ K the equation of state becomes

$$l - a \approx \frac{2a}{3}\,\frac{\theta^2}{\theta_c^2+\theta^2}, \tag{16}$$

where θ_c is defined by the relationship $\phi^{1-\lambda} = \theta_c^2$. This gives rise to a "critical pressure" $P_c = 3\epsilon(\lambda-1)/2a$. It is then evident that the zero temperature limit of volume per particle is a discontinuous function of θ,

$$l = \begin{cases} a, & P > P_c; \\ 4a/3, & P = P_c; \\ 5a/3, & P < P_c. \end{cases} \tag{17}$$

Physically, these three possibilities correspond to all the particles being in the inner well, in both wells with equal probability, or in the outer well. At zero pressure and $T = 0$ K, the system exists in a crystalline state with all the particles in the deeper, outer well, with $l = 5a/3$. Of course, as soon as the temperature is different from zero, the discontinuity in volume disappears and, as is normal for any substance, the volume is a continuous monotonically decreasing function of the pressure. The application of pressure simply forces the particles into greater confinement, in this case into the inner well, creating a higher overall density, as in the dense ice polymorphs of the real system.

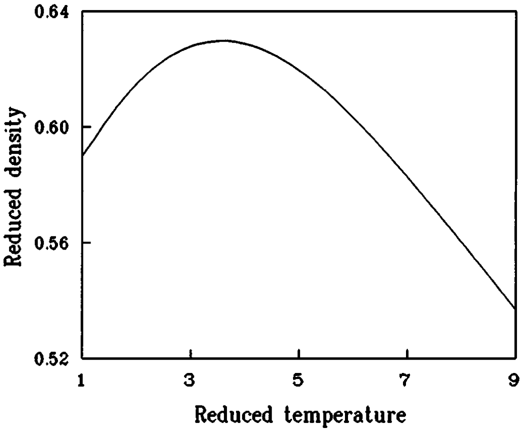

FIG. 1. The reduced density $\rho a/m$ as a function of reduced temperature k_BT/ϵ for $\lambda = 10$ and for $P = 10\epsilon/a$ for the double well model. For explanation of symbols, see text.

More interesting are temperature changes for pressures lower than critical. Keeping the pressure fixed at not too high a value and raising the temperature from $T = 0$ K causes particles in the outer well to "boil" into the inner well, increasing the overall density. This effect, followed by the inevitable expansion at high temperatures, then produces a density maximum. As a specific example, we choose $\lambda = 10$ and $P = 10\epsilon/a$. Since this pressure is less than the critical pressure, which equals $13.5\epsilon/a$, a density maximum is obtained. This is seen in Fig. 1, where $\rho a/m$ is plotted as a function of k_BT/ϵ.

Though it is, of course, unrealistic to compare $\rho(T)$ for the one-dimensional model with that of real water, it is of interest to note that by appropriate parameter scaling of the one-dimensional result, it is possible to match *exactly* the $\rho(T)$ curve of real liquid water at both normal and elevated pressures. There is thus no doubt that this can also be done for a three-dimensional computational model for water. In fact, increasing the pressure in the one-dimensional model shows that the density maximum becomes broader and shifts to lower temperatures, finally disappearing sufficiently high pressures. This is exactly the type of behavior observed in the real liquid [18].

In summary, it has been shown that by mapping the two known second neighbors in real liquid water onto first-neighbor locations in a one-dimensional model a density maximum is obtained. The one-dimensional model also captures other pressure-temperature properties of this mysterious and important liquid. Since realistic density maxima are clearly absent in popular computational water models [4,5], it might be necessary, in order to reproduce the known temperature and pressure effects, to insert empirically the appropriate double-well feature into the water-water potential. Three-dimensional studies along these lines are currently taking place in our laboratory [19].

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