LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 July 2002 issue.

COMMENTS

Comment on "Observations on an equation of state for water confined in narrow slit-pores" [J. Chem. Phys. 116, 2565 (2002)]

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We recently introduced a molecular thermodynamic theory[1] for bulk water, which has been extended[2] to study films confined between planar surfaces. Giaya and Thompson[3] have investigated some of its predictions at 25 °C. They make several observations and suggest a strategy for extending the theory to allow molecules to participate in multiple hydrogen bonds (h-bonds). However, their treatment does not explicitly account for the orientational degrees of freedom of the molecules. We explain why this prevents the theory from capturing the thermodynamic anomalies that distinguish water from simpler liquids. We also clarify some of their observations concerning the theories of Refs. 1 and 2.

The theory presented in Ref. 1 can qualitatively predict many of water's distinctive thermodynamic properties, including its anomalous temperature dependencies of density ρ, isothermal compressibility κ_T, and isobaric heat capacity c_P. Understanding why the theory can predict the density maximum is of particular importance because of its thermodynamic connection to water's other unusual properties.[4,5] The key is that it incorporates, in a schematic way, two important features of h-bonding in water: h-bonds (1) restrict the orientations of participating molecules (lowering the entropy s) and (2) favor low coordination numbers (lowering the density ρ). Thus, as in liquid water,[6] the extent of h-bonding in the theory depends on temperature T: energy favors the formation of h-bonds at low T, but entropy opposes their formation at high T. Cooling the "cold" liquid creates open h-bonded structures, while cooling the "warm" liquid creates denser, nonbonded molecular arrangements. The density maximum at 1 bar occurs at $T=4\,°C$ where these competing tendencies balance.

A limitation of our theory, explicitly acknowledged in the title of Ref. 1, is that only one h-bond per molecule can be formed. However, by accounting in an approximate manner for h-bond cooperativity through the above-mentioned positive correlation between ρ and s, the theory is nevertheless able to capture many of water's distinctive thermodynamic anomalies.

Giaya and Thompson[3] have proposed to improve the h-bonding interactions presented in Ref. 1. This is an important challenge that seems necessary for advancement toward a comprehensive theory of water. In particular, they propose to allow molecules to form four h-bonds with their neighbors. However, their treatment does not explicitly account for water's orientational degrees of freedom. Hence, the entropic penalty that should arise from the orientational constraints of bonding is absent. Their Helmoltz free energy (see Eq. (19) of Ref. 3) can be expressed as $f(T,v)=f_{\mathrm{vdW}}(T,v)+f_{\mathrm{HB}}(v)$, where $f_{\mathrm{vdW}}(T,v)$ is the van der Waals contribution, $f_{\mathrm{HB}}(v)$ is the h-bonding contribution, and v is the molar volume. Note that T does not influence the h-bonding term $f_{\mathrm{HB}}(v)$. As a result, h-bonding does not affect the entropy $s(T,v)=-(\partial f/\partial T)_v=s_{\mathrm{vdW}}(T,v)$. In Ref. 1, we show that models that have this form cannot predict water's density anomalies. While Giaya and Thompson acknowledge that they ignore the T-dependence of h-bonds, the above-given simple analysis shows the consequences of this omission. Thus, although we agree that improving the h-bonding interactions of Refs. 1 and 2 is an important goal, the strategy suggested by Giaya and Thompson produces a theory that cannot describe, even qualitatively, many of water's distinctive thermodynamic properties.

Giaya and Thompson also offer observations about the theories of Refs. 1 and 2, several of which we clarify in the following. Their first observation is that the h-bonds do not affect the vapor–liquid coexistence curve. The second observation is that the h-bonding contribution to the free energy is not sensitive to density ρ. Although these observations are valid at high T, they do not apply at low T, as explained in the following.

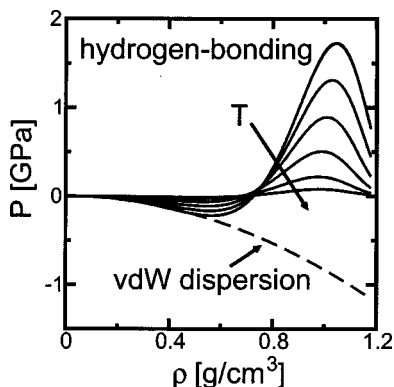H-bonding impacts the vapor–liquid coexistence curve.

FIG. 1. H-bonding (solid lines) and vdW dispersion (dashed line) contributions to pressure P vs density ρ for the model of Ref. 1. The parameters are those that give rise to the two-critical-point scenario (Ref. 1). The dispersion contribution does not depend on temperature T. The h-bonding contribution is shown for $T = 50, 100, 150, 200, 250,$ and 300 K.
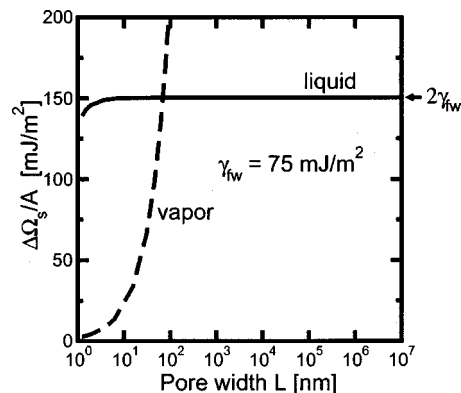

FIG. 2. The excess grand potential per unit area $\Delta\Omega_s/A$ vs pore width for the liquid (solid line) and the vapor (dashed line) films between two hard walls. The bulk phase is at temperature $T = 25\,°C$ and pressure $P = 28.4$ bar. A more detailed plot appears in Fig. 8 of Ref. 2. γ_{fw} is the effective surface tension between the fluid and a hard wall.

This can be seen by comparing the phase diagram of our theory (Fig. 5 in Ref. 2) to that of the model with its h-bonds "turned off," i.e., the confined van der Waals fluid (e.g., Fig. 2 in Ref. 7). Specifically, h-bonds cause the density of the liquid branch to exhibit a maximum as a function of T (i.e., creating a "nose" in the $P-T$ plane). This prediction, although exaggerated in its magnitude, is in qualitative agreement with water's phase diagram. Moreover, the h-bonding contribution to the Helmholtz free energy f can be sensitive to changes in density ρ. The experimentally accessible quantity that describes the relationship between f and ρ is the pressure $P = \rho^2[\partial f/\partial\rho]_T$. In Fig. 1, we plot the contributions of vdW attractions and h-bonds to P. We see that h-bonds are important at low T, but that their contribution decreases appreciably as T is increased.

Although the two observations of Giaya and Thompson do not apply for arbitrary T, they are valid at $T = 25\,°C$, a temperature where one would expect h-bonds to have a more significant effect. Thus, they have identified an important shortcoming of the theory as it is presented in Refs. 1 and 2: the h-bonding interactions attenuate too rapidly with T [this is also evidenced by Fig. 3(c) of Ref. 1]. Nevertheless, the theory captures qualitatively many *thermodynamic consequences of hydrogen-bonding* in the stable liquid range, including maxima in ρ (Fig. 7 of Ref. 3) and minima in κ_T and c_P (Fig. 7 of Ref. 2). Moreover, its parameters were chosen to capture qualitatively water's anomalies and its global phase diagram, not to accurately reproduce water's equation of state at $25\,°C$. We do not know how well Giaya and Thompson's modified version will describe water's equation of state or other measurable properties, since they do not present comparisons in Ref. 1 with the available experimental data.

Finally, Giaya and Thompson use the theory of Ref. 2 to consider the stability of a water film confined between two hydrophobic plates of area A separated by pore width L. The thermodynamically stable pore phase is the one that minimizes the grand potential $\Omega = -P_\| AL$, where $P_\|$ is the transverse component of the pressure tensor. Following Ref. 2, they construct a plot of the excess grand potential per area

$\Delta\Omega_S/A = -(P_\| - P)L$ versus pore width L, where P is the pressure of the bulk phase that imposes its temperature T and chemical potential μ on the pore phase. They show calculations and present arguments that incorrectly indicate that $\Delta\Omega_S/A \to 0$ at very large pore widths ($L \approx 10^5$ nm).

For large L, the effect of confinement is to create two fluid–wall interfaces of area A, the free energy cost of which is $2\gamma_{fw}A$, where γ_{fw} is the effective fluid–wall surface tension. Thus, the quantity $\Delta\Omega_S/A$ does not decay to zero; rather it approaches the well-known asymptote $\Delta\Omega_S/A \to 2\gamma_{fw}$. This asymptote can be derived analytically[8] and we show in Fig. 2 that it is in fact generated by the theory of Ref. 2. Our predicted fluid–wall surface tension $\gamma_{fw} = 75$ mJ/m^2 is close to water's experimental vapor–liquid surface tension $\gamma_{vl} = 72$ mJ/m^2 at $25\,°C$, a prediction that was anticipated earlier by Stillinger.[9]

The calculation of Giaya and Thompson does not reproduce this behavior, and we can only assume that it is an artifact of their numerical solution. In fact, they claim that the theory of Ref. 2 is prone to precision errors. We have not found that it poses unusual numerical problems. Note that determining $P_\|$ does require the simultaneous solution of nonlinear algebraic equations. However, the methods required for solving such equations are relatively standard and are analogous to those used to calculate the liquid–vapor coexistence curves of other simple analytical models for fluids.

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