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# Removal of Estrone From Water by Adsorption on Zeolites with Regeneration by Direct UV Photolysis

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# Observations on an equation of state for water confined in narrow slit-pores

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Water may be adsorbed in microporous or mesoporous materials from the liquid phase or from the gaseous, or vapor, phase. In either case, the fluid state of the adsorbed water molecules may be liquid or vapor as well, depending on several factors inherent to the adsorbate itself. This work sought to understand these factors using an equation of state reported in the literature recently. It was determined that the model's predicted contribution of the hydrogen bonding to the Helmholtz free energy was less than expected. The estimation of the magnitude of hydrogen bonding appears to be more realistic if positive contributions of four neighbors is included rather than one. The model also appears to involve quite sensitive calculations, which may be prone to precision errors. © 2002 American Institute of Physics. [DOI: 10.1063/1.1432318]

## I. INTRODUCTION

A variety of microporous and mesoporous materials are of interest in water treatment and (humid) gas cleaning applications. Membrane separation systems taking advantage of microporous or mesoporous materials are increasingly being investigated. As such, it is of interest to understand how water molecules interact with the pore walls in these materials, and how hydrogen bonding affects water retention from the vapor or liquid phases.

Zhao *et al.*<sup>1</sup> studied the adsorption of several volatile organic compounds on MCM-41, dealuminated NaY, and Silicalite-1 samples. They found that the adsorbents's capacity correlated to the pore volume, i.e., the materials having the highest pore volume also had the highest capacity for the sorbates. The same was not true when the adsorption of trichloroethylene out of liquid phase was studied.<sup>2</sup> Surprisingly, the sample with smaller pore dimensions and volume (Silicalite-1) outperformed dealuminated NaY and MCM-41<sup>3</sup> materials. It was suggested<sup>2</sup> that liquid water cannot form inside the small hydrophobic pores of Silicalite-1, while it was possible for liquid water to form inside the DAY and other mesoporous materials. This assumption was later proven experimentally.<sup>3</sup> The differences in the confined water phase were suspected to be the main reason for differences in adsorption properties of those materials.

Therefore, understanding the behavior of waterlike fluids confined in micro- and mesopores is of great practical and theoretical importance. Answering these two questions was especially important to us: Is it possible that very small variations in the pore size (such as those noted between Silicalite and NaY samples) can cause big changes in the density of the confined phases? Is it possible to shift liquid-vapor phase diagram by modifying fluid-wall interactions, such that vapor will be the stable phase even for relatively large pores?

Evans<sup>4</sup> and Kohlmeyer *et al.*<sup>5</sup> have reviewed theoretical

and computational treatments of pore fluids. Molecular dynamics and Monte Carlo simulations are often used for theoretical studies of confined fluids. These methods are perhaps most exacting, but also most computationally intensive. On the other hand, methods that involve the mean-field approximation are less exact, but also less computationally demanding. Diestler and Schoen,<sup>7</sup> and more recently, Schoen and Diestler<sup>6</sup> and Truskett *et al.*<sup>8</sup> studied the behavior of a confined fluid based on the mean-field theory. Schoen and Diestler<sup>6</sup> studied the thermodynamic behavior of a nonassociating fluid confined to a slit-pore, applying the perturbation theory. Truskett *et al.*<sup>8</sup> extended that approach to include fluid-fluid hydrogen bonding interactions, thus providing an equation of state for water confined in narrow slit-pores. Their equation accounts for fluid-fluid, fluid-wall, and hydrogen bonding interactions. The Truskett *et al.* work<sup>8</sup> sought to investigate the global phase behavior of water in restricted geometries. That in turn could allow that confinement to be used for studying the hypothesis of liquid-liquid transition of water, or the two-critical point scenario for water.

It is believed that the model presented by Truskett *et al.*<sup>8</sup> has the potential of being applied in many other scenarios where confined water is involved and can be used to predict whether the confined fluid is liquid- or vaporlike. Encouraged by the results presented in their papers,<sup>8,9</sup> we analyzed their model in some detail with a view toward using it to analyze data reported recently.<sup>2</sup> However, we noticed that the model presented by Truskett *et al.*<sup>8</sup> was not quite suitable when water at ambient conditions (such as those of interest to adsorption experiments) was studied. As shown below, the parameters used by Truskett *et al.*,<sup>8</sup> which although seemed to be suitable for a general description of the phase behavior of water, were not appropriate for describing liquid and vapor phases at ambient conditions. Additionally, we noticed the following:

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- (i) The hydrogen bond strength predicted by the Truskett *et al.*<sup>8</sup> model did not influence the liquid–vapor coexistence curve for the confined fluid;
- (ii) the hydrogen bonding contribution to the Helmholtz free energy hardly changes with density (even as density goes to zero);
- (iii) the expression used by the Truskett *et al.*<sup>9</sup> model to calculate the number of neighbors implies that at least one of the molecules participating in the hydrogen bonding has a cavity surrounding it. This seems to pose a problem describing liquid water at normal density;
- (iv) the Truskett *et al.*<sup>8,9</sup> model assumes that water molecules form only one hydrogen bond. Here a model that accounts for up to four hydrogen bonds per molecule is proposed.

Conscious that it is not possible to have a universal model capable of reproducing all features of bulk and confined water at a wide range of temperature and pressure, we analyzed the Truskett *et al.* model<sup>8,9</sup> with the intention of making necessary modifications to apply it for bulk and confined water at ambient conditions.

## II. MODEL SUMMARY

The details of the model for the equation of state are given in the recent papers by Truskett *et al.*,<sup>8,9</sup> and will not be repeated here. However, briefly, the development begins with a definition of the Helmholtz free energy for water molecules confined in narrow slit-pores, which is taken as the logarithm of the canonical partition function,  $Q$ . The canonical partition function depends on the fluid–fluid, fluid–wall, and hydrogen bonding interactions, in addition to the physical properties of water molecules.

Specifically, the Helmholtz free energy was given by Eq. (3.32), reported previously<sup>8</sup>

$$F = -N\beta^{-1} \left[ \ln \left( \frac{1 - \rho_p b(\zeta)}{\rho_p \Lambda^3} \right) + 1 \right] - N a_p(\zeta) \rho_p - N \Psi_p(\zeta) - N \beta^{-1} \left[ \ln(4\pi) + \sum_{j=1}^8 p_j^{\text{pore}}(\rho_p, \zeta) \ln f_j \right], \quad (1)$$

where  $N$  is the number of molecules in the system,  $\beta = 1/kT$ ,  $\rho_p$  is the fluid density in the pores,  $b(\zeta)$  is the van der Waals excluded volume of the fluid molecules,  $a_p(\zeta)$  is the parameter for fluid–fluid dispersion interaction for the pore fluid,  $\Psi_p(\zeta)$  is the parameter for the fluid–wall interaction function,  $p_j^{\text{pore}}(\rho_p, \zeta)$  is the probability that, in a hard-sphere fluid at a given density, a given hard sphere has a cavity of radius  $r_i$  surrounding it and that  $j$  other sphere centers lie within its hydrogen-bonding shell, and the function  $f_j$  was given by<sup>8</sup>

$$f_j = \left[ 1 + \frac{j}{4} (\cos \phi^*)^2 (\exp \beta \epsilon_j - 1) \right], \quad (2)$$

where the hydrogen-bond energy was given by<sup>8,9</sup>

$$\epsilon_j = \epsilon_{\text{max}} - (j-1) \epsilon_{\text{pen}}. \quad (3)$$

From the thermodynamic treatment of the confined fluid, the differential form of the Helmholtz free energy for the confined fluid is given<sup>8</sup> as

$$dF = -SdT - P_{\parallel}LdA - P_{zz}AdL + \mu dN. \quad (4)$$

The chemical potential of the fluid contained inside the pores is found from the derivative of the Helmholtz free energy with respect to the number of molecules,  $N$ , at constant temperature  $T$ , area  $A$ , and slit separation  $L$  [ $(\partial F/\partial N)_{T,A,L}$ ]<sup>6</sup> [see Eqs. (1) and (4)]. For a waterlike fluid, one can find the following expression for the chemical potential for the fluid in the pores:

$$\begin{aligned} \mu_p = & \beta^{-1} \ln \left( \frac{\rho_p \Lambda^3}{1 - \rho_p b(\zeta)} \right) + \beta^{-1} \frac{b(\zeta) \rho_p}{1 - \rho_p b(\zeta)} - 2a_p(\zeta) \rho_p \\ & - \Psi_p(\zeta) - \beta^{-1} \left[ \ln(4\pi) + \sum_{j=1}^8 p_j^{\text{pore}}(\rho_p, \zeta) \ln f_j \right. \\ & \left. + \rho_p \sum_{j=1}^8 \frac{\partial p_j^{\text{pore}}(\rho_p, \zeta)}{\partial \rho_p} \ln f_j \right]. \end{aligned} \quad (5)$$

The chemical potential of the fluid outside the pores is computed by finding the limiting value in Eq. (5) for the chemical potential inside the pores as the pore dimension,  $L$ , goes to infinity. Therefore, the chemical potential of the bulk fluid is given by

$$\begin{aligned} \mu_b = & \beta^{-1} \ln \left( \frac{\rho_b \Lambda^3}{1 - \rho_b b_b} \right) + \beta^{-1} \frac{b_b \rho_b}{1 - \rho_b b_b} - 2a_b \rho_b \\ & - \beta^{-1} \left[ \ln(4\pi) + \sum_{j=1}^8 p_j^{\text{bulk}}(\rho_b) \ln f_j \right] \\ & - \beta^{-1} \rho_b \sum_{j=1}^8 \frac{\partial p_j^{\text{bulk}}(\rho_b)}{\partial \rho_b} \ln f_j. \end{aligned} \quad (6)$$

Our focus was on finding the density of the stable phase inside the pores for a given state of the external bulk fluid, as the pore width was varied. For a given temperature and density of the bulk fluid, its chemical potential was calculated using Eq. (6). Equilibrium is established when the chemical potential of the fluid (liquid or vapor water) outside the pores is equal to the chemical potential of the fluid (liquid or vapor) confined in the micro- or mesopores. Therefore, at fixed system parameters, the value of the chemical potential of the fluid inside the pores (at equilibrium) is known as well. Solving Eq. (5) for  $\rho_p$  yields, in most cases, three real solutions. The value of  $\rho_p$  which minimizes the excess grand potential per unit area,  $\Delta\Omega_s/A = -(P_{\parallel} - P^{\text{bulk}})L$ , must be selected to determine the stable water phase confined in the pores. Using Eqs. (1) and (4) one can find the pressure as the derivative of the Helmholtz free energy with respect to  $A$  at constant  $T$ ,  $L$ , and  $N$ . The fluid pressure in the pores is, therefore, given as<sup>8</sup>

$$\begin{aligned} P_{\parallel} = & \frac{\rho_p}{\beta(1 - \rho_p b_p(\zeta))} - a_p(\zeta) \rho_p^2 \\ & - \frac{\rho_p^2}{\beta} \sum_{j=1}^8 \left( \frac{\partial p_j^{\text{pore}}(\rho_p)}{\partial \rho_p} \right)_{T,\zeta} \ln f_j. \end{aligned} \quad (7)$$

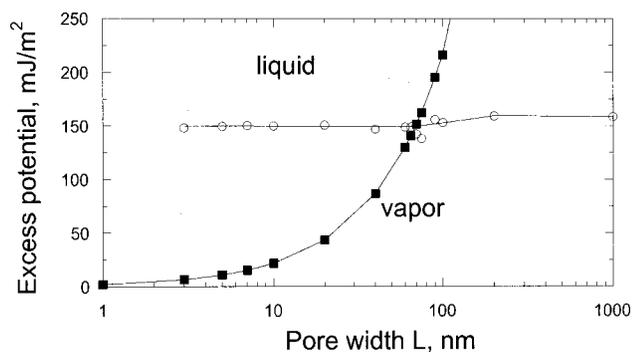


FIG. 1. The excess grand potential vs pore width for the liquid and vapor at 298 K and  $\mu = -38.57$  kJ/mol confined between two hard plates,  $\epsilon_{fw} = 0$ .

### III. RESULTS

Figure 8 in Truskett *et al.*<sup>8</sup> shows the excess grand potential per unit area vs pore width for the liquid and vapor phases. The bulk liquid outside the pores has a fixed chemical potential of  $-183.56$  kJ/mol at a temperature of 298 K. Under these conditions, the authors calculated the bulk pressure to be 28.4 bar. The point at which the liquid and vapor curves intersect marks the slit-width at which the stable fluid changes between being vaporlike to being liquidlike. According to their figure, for slit pore widths smaller than  $\sim 68$  nm the stable phase inside the slit pores was predicted to be vapor, and for width  $> 68$  nm liquid was the predicted stable phase inside the pores.

We tried to reproduce their Fig. 8; the results are shown here in Fig. 1 which seems to be in fairly good agreement with their Fig. 8. Figure 1 was derived based on a bulk fluid at a temperature of 298 K and density of  $0.99914$  g/cm<sup>3</sup>. Under these conditions the pressure was calculated to be 28.4 bar (the same as in the Truskett *et al.* papers<sup>8,9</sup>), but the chemical potential was  $-38.57$  kJ/mol, i.e., very different from the value of  $-183.56$  kJ/mol reported by Truskett *et al.*<sup>8</sup> [Truskett<sup>10</sup> attributed the difference in the chemical potential to the different values of the wavelength  $\Lambda$ . In this work, the wavelength parameter was estimated as  $\Lambda = h/\sqrt{2\pi mkT}$ ,<sup>11</sup> whereas, Truskett *et al.*<sup>8,9</sup> did not include  $m$  (the mass of water molecules) in the wavelength evaluation. These differences in the estimation of  $\Lambda$  do not affect the equation of state or the phase diagram.] Thus, the results shown in Fig. 1 are essentially the same as the results shown in Fig. 8 by Truskett *et al.*<sup>8</sup>

Figure 1 (as well as Fig. 8 in Truskett *et al.*<sup>8</sup>) might give the impression that for the stable phase, as the pore width goes to infinity, the excess grand potential per unit area goes to a constant different from zero ( $\sim 150$  mJ/m<sup>2</sup>). One would expect that, for sufficiently large  $L$ , the fluid inside the pores should become indistinguishable from the bulk fluid outside the pores. Therefore, the excess grand potential should go to zero. The excess grand potential values of the liquid phase for larger slit widths, plotted in Fig. 2, show that the excess grand potential does indeed go to zero, as  $L$  gets larger. However, the slit width required for this convergence appears to be somewhat larger than expected on the basis of the size of water molecules, the hydrogen bonding clusters, and typical fluid-wall interaction distances.<sup>12</sup> Berard *et al.*<sup>13</sup> also

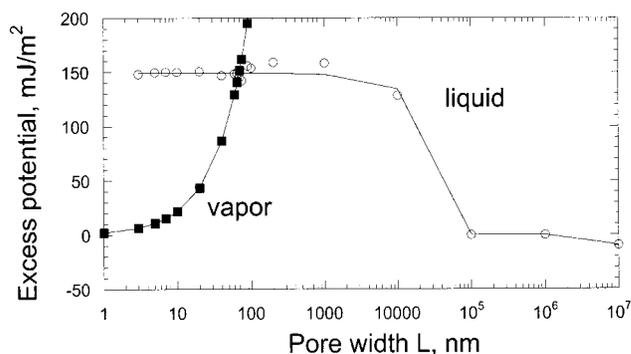


FIG. 2. The excess grand potential for the vapor and liquidlike phases inside the pores for larger plate separation. The excess potential goes to zero for very large  $L$ .

showed that at large plate separations, the pressure of the fluid confined between two plates equals the bulk pressure. Despite these subtle differences, the main feature of Fig. 8 in Truskett *et al.*<sup>8</sup> (i.e., the existence of a pore width for which there is a transition from vapor to liquid phase inside the pores) was reproduced.

To evaluate the influence of hydrogen bonding in the confined fluid behavior, we recomputed the excess potential without the hydrogen bonding interactions. Keeping the pressure and temperature of the bulk fluid the same as previously, we recalculated the excess grand potential for liquid and vapor phases for various pore widths. The phase with the lower excess grand potential, shown in Fig. 3(a), should be the stable phase. The filled symbols are for the liquid phase, and the open symbols are for the vapor phase. The two curves show that the predicted effect of hydrogen bonding is not significant insofar as these computations are concerned. As expected, the vapor phase curves were identical for both cases, i.e., with and without hydrogen bonding. In the vapor phase, in accord with the mean-field theory, molecules are too far apart to interact via hydrogen bonding (the average distance between molecules in the vapor phase is  $\sim 200$  times larger than the hydrogen bonding shell radius). However, surprisingly, in the liquid phase, hydrogen bonding was not predicted to cause a significant change either. Even more surprisingly, the small change was in the opposite direction to that which one could expect. Confinement disrupts the fluid-fluid hydrogen bonding, so the minimum pore width for which liquid can be the stable phase inside the slit-pore, will shift to lower values as hydrogen bonding is "turned off." That is another reason that prompted modifications to the original model.<sup>8</sup> It is observed that the intersections with and without hydrogen bonding are very close to one another. Similar results are also plotted in Fig. 3(b), with the results from the model with and without the hydrogen bonding effect.

The data are plotted in another format in Fig. 3(b), i.e., the density of the stable pore phase versus pore width. The predicted results with hydrogen bonding included are shown by the solid line in Fig. 3(b). The results in that figure indicate that as the pore width is decreased, there is a critical dimension at which the confined fluid changes abruptly from liquidlike to being a vaporlike fluid. The density of the stable

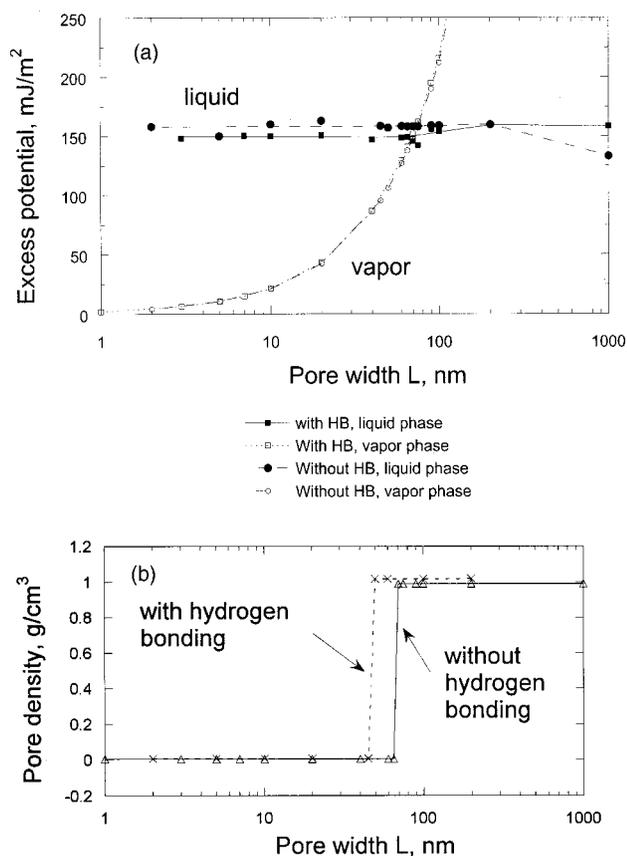


FIG. 3. The excess grand potential (a) and density of the stable phase (b) for porous fluid. Results were derived based on equation of state presented by Truskett *et al.* (Ref. 8) for the case with and without hydrogen bonding.

phase without hydrogen bonding included is plotted against the slit-width,  $L$ , in Fig. 3(b) with the dotted line. The critical slit-widths for both cases are observed to be essentially the same, i.e., about 50–70 nm.

In other words, according to the model presented by Truskett *et al.*<sup>8,9</sup> the influence of hydrogen bonding in determining the state of the fluid confined in micropores or mesopores is not an important force. This conclusion was not what one would expect, so further investigations to understand these results were undertaken.

First, it was puzzling why the conditions for Fig. 8 in Truskett *et al.*<sup>8</sup> were such that the pressure was 28.4 bar (and not 1 bar, for example). Plotting pressure versus density, one can note from Fig. 4 that very small changes in density values can produce significant changes in the pressure of the liquidlike bulk fluid. That is, as one would expect, large changes in pressure can be expected to cause only minor changes in fluid (liquid) density, and this is reflected in the very steep functional relationship of pressure changes with fluid density seen in Fig. 4. In this case changing the pressure from 1 bar to 28 bar only results in a 0.1% change in the fluid density. This observation suggests that obtaining accurate values of the fluid pressure from fluid density may be very difficult and prone to numerical inaccuracies. It is then easy to comprehend why small errors in the computation of the fluid density can lead to large errors in estimating the pressure. Instead of picking a value for density and calculat-

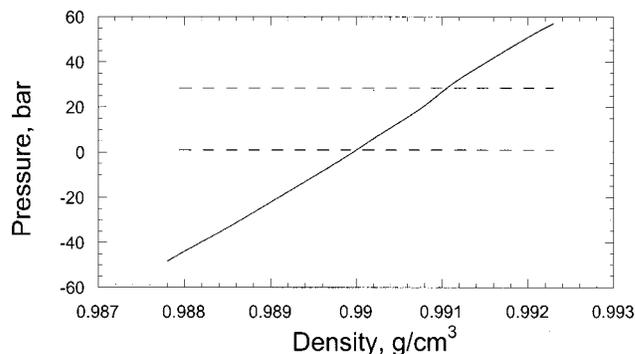


FIG. 4. Sensitivity of the pressure of the bulk liquid with density. Horizontal lines represent pressure of 1 and 28.4 bar.

ing the pressure and chemical potential, and so forth, we wanted to find the density for which, under the parameters used by Truskett *et al.*<sup>8,9</sup> the Gibbs free energy would be at its minimum for 1 bar and 298 K.

Using the relation of the Gibbs free energy with the Helmholtz free energy one can find

$$G = -N\beta^{-1} \left[ \ln \left( \frac{1 - \rho_b b_b}{\rho_b \Lambda^3} \right) + 1 \right] - N a_b \rho_b - N\beta^{-1} \left[ \ln(4\pi) + \sum_{j=1}^8 p_j^{\text{bulk}}(\rho_b) \ln f_j \right] + N \frac{P}{\rho}. \quad (8)$$

At a given pressure, the fluid will attain the density for which the Gibbs free energy is a minimum, as shown in Fig. 5. For the parameter values given by Truskett *et al.*<sup>8</sup> that density value was calculated to be 0.990 g/cm<sup>3</sup>. For this value of the liquid density, the corresponding chemical potential was  $-38.61$  kJ/mol. Solving Eq. (6) for the fluid density, using  $-38.61$  kJ/mol for the chemical potential, three solutions were found: 0.433 g/cm<sup>3</sup>,  $4.948 \cdot 10^{-3}$  g/cm<sup>3</sup>, and 0.990 g/cm<sup>3</sup>. The stable phase would be the one that has the minimum grand potential; in this case the vapor phase turned out to be the stable phase. In other words, for the parameter values used by Truskett *et al.*<sup>8</sup> the bulk fluid is predicted to be in the vapor phase at 298 K and 1 bar, while it is known that the stable phase of water for these conditions should be

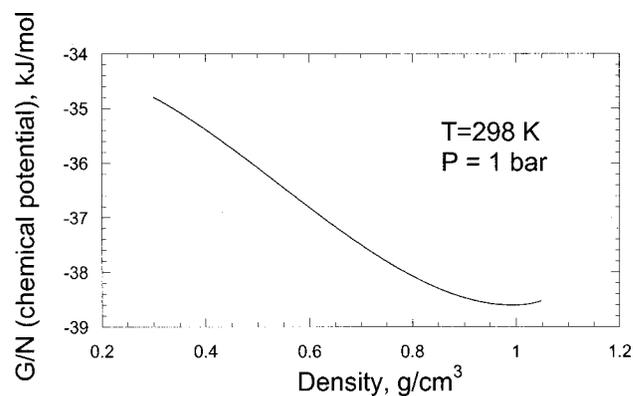


FIG. 5. Change of the Gibbs free energy with density for a fluid at 298 K and 1 bar. The minimum Gibbs free energy at these conditions is reached at density 0.990 g/cm<sup>3</sup>.

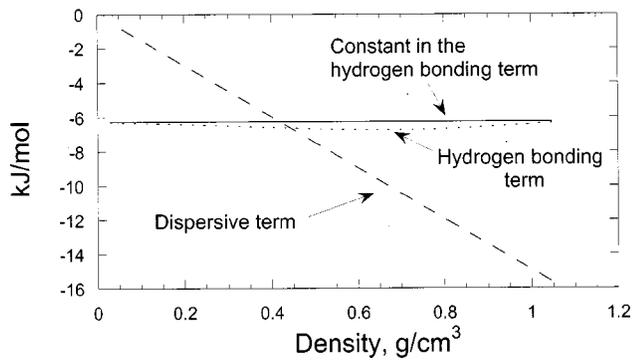


FIG. 6. Contribution of the hydrogen bonding and dispersive interactions to the Helmholtz free energy, using the Truskett *et al.* model (Refs. 8 and 9).

liquid. Therefore, some of the parameter values chosen in Truskett *et al.*,<sup>8,9</sup> while giving a reasonable global description of water’s phase behavior, may not be appropriate for water at 298 K and 1 bar, as noted by Truskett.<sup>14</sup>

It is suggested here that a better way to determine the values for  $a_b$  and  $b_b$  would be to require for the bulk fluid that

$$\begin{aligned} P(\text{bulk liquid}) &= 1 \text{ bar}, \\ P(\text{saturated vapor at } 298 \text{ K}) &= P_{\text{sat}}, \\ \mu(\text{vapor,sat}) &= \mu(\text{liquid}). \end{aligned} \quad (9)$$

In other words, the first condition requires that bulk liquid attains the normal density ( $\sim 1 \text{ g/cm}^3$ ) at 1 bar and 298 K; the second condition requires that saturated vapor phase at 298 K attains the saturated pressure of water, and the third condition requires that vapor and liquid phase coexist at 298 K and 1 bar. Lum *et al.*<sup>15</sup> also defined parameters for their model based on the vapor-liquid coexistence at 298 K. Besides the choice of parameters, several comments regarding the hydrogen-bonding model itself come to mind:

(1) Applying Eq. (1) for infinitely large  $L$  one finds the expression for the Helmholtz free energy for the bulk fluid

$$\begin{aligned} F = -N\beta^{-1} & \left[ \ln \left( \frac{1 - \rho_b b_b}{\rho_b \Lambda^3} \right) + 1 \right] - N a_b \rho_b - N\beta^{-1} \left[ \ln(4\pi) \right. \\ & \left. + \sum_{j=1}^8 p_j^{\text{bulk}}(\rho_b) \ln f_j \right]. \end{aligned} \quad (10)$$

If we analyze the term which introduces the contribution of hydrogen bonding into the Helmholtz free energy, i.e., the last term in the above equation, we observe that it contains a constant  $[\ln(4\pi)]$  and a term which depends on the number of molecules in the hydrogen bonding shell. This expression suggests that there is constant contribution of hydrogen bonding to the Helmholtz free energy, i.e., independent of the fluid density. In fact, one would expect, that for low enough densities, the hydrogen bonding should not contribute to the energy of the system. Furthermore, when the two terms were calculated, it was noticed that the contribution from the second term was insignificant, regardless of the fluid density, compared to the constant  $[\beta^{-1} \ln(4\pi)]$ . These results are shown graphically in Fig. 6. However, the con-

stant term and the total hydrogen bonding term are essentially the same, suggesting that all other terms in the hydrogen bonding contribution are insignificant. Note as well that the total hydrogen bonding contribution hardly changes with fluid density, which seems peculiar, especially at very low fluid densities in which water molecules would be too far apart to participate in hydrogen bonding to a significant extent.

(2) When present as in liquid water, the hydrogen bonding energy is known to be significant compared to van der Waals interactions. However, when the fluid–fluid interaction energy was compared to the hydrogen bonding energy for the parameters given by Truskett *et al.*,<sup>8,9</sup> the dispersive term was the dominant term for densities above  $0.5 \text{ g/cm}^3$  as seen in Fig. 6. The dispersion term is noted to become less (negative) important as the fluid density becomes very small, as expected.

(3) Recall that  $p_j^{\text{bulk}}(\rho_b)$  is the probability that, in a hard-sphere fluid at a given density, a given hard sphere in the bulk fluid has a cavity of radius  $r_i$  surrounding it and that  $j$  other sphere centers lie within its hydrogen-bonding shell. Truskett *et al.*<sup>8,9</sup> suggested the expression for  $p_j^{\text{bulk}}$  as follows:

$$p_j^{\text{bulk}}(\rho_b) = p(r_i, 0) \cdot p(r_0, j/r_i). \quad (11)$$

The first quantity,  $p(r_i, 0)$ , is the probability that a given sphere has a cavity of radius  $r_i$  surrounding it. The second term,  $p(r_0, j/r_i)$ , is the conditional probability that there are exactly  $j$  particles in the sphere’s hydrogen bonding shell ( $r_i \leq r \leq r_0$ ). The expressions for probabilities are given, respectively,<sup>9</sup> as

$$p(r_i, 0) = \exp \left( - \frac{24\eta_b}{\sigma_f^3} \int_{\sigma_f}^{r_i} r^2 G(r) dr \right) \quad (12)$$

and

$$\begin{aligned} p(r_0, j/r_i) &= \frac{1}{j!} \left( \frac{24\eta_b}{\sigma_f^3} \int_{\sigma_f}^{r_0} r^2 G(r) dr \right)^j \\ & \times \exp \left( - \frac{24\eta_b}{\sigma_f^3} \int_{\sigma_f}^{r_0} r^2 G(r) dr \right), \end{aligned} \quad (13)$$

where

$$G(r) = \begin{cases} 0 & r \leq \sigma_f \\ a_0 + \frac{a_1}{(r/\sigma_f)} + \frac{a_2}{(r/\sigma_f)^2} & r \geq \sigma_f \end{cases} \quad (14)$$

and

$$\begin{aligned} a_0 &= 1 + 4\eta_p G(\sigma_f), \\ a_1 &= \frac{3\eta_p - 4}{2(1 - \eta_p)} + 2(1 - 3\eta_p)G(\sigma_f), \\ a_2 &= \frac{2 - \eta_p}{2(1 - \eta_p)} + (2\eta_p - 1)G(\sigma_f), \end{aligned} \quad (15)$$

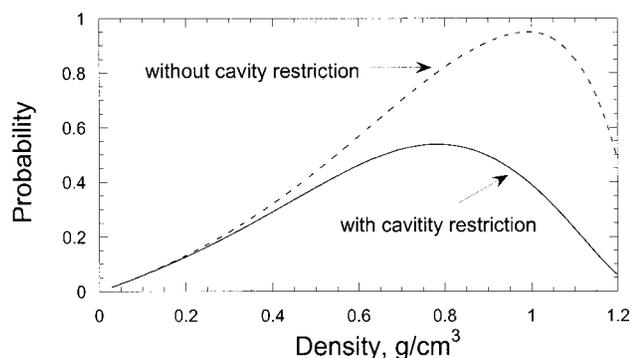


FIG. 7. Probability that a molecule participates in hydrogen bonding. Solid line calculated from the model presented by Truskett *et al.* (Ref. 8 and 9). Dashed line results from dropping the requirement for a cavity around the central molecule.

$$G(\sigma_f) = \frac{1 - \eta_p/2}{(1 - \eta_p)^3},$$

$\eta_b$  is the packing fraction, which for bulk fluid is defined as

$$\eta_b = \frac{\pi \sigma_f^3}{6} \rho_b. \quad (16)$$

It follows from their treatment, although not explicitly, that the probability ( $P_{HB}$ ) that a molecule can participate in hydrogen bonding is given by

$$P_{HB} = \sum_{j=1}^8 p_j^{\text{bulk}}(\rho_b). \quad (17)$$

In Fig. 7 this probability is plotted against the fluid density as shown by the solid line. The results show that the highest probability that a molecule can participate in hydrogen bonding is 55% and this value was obtained for fluid density of  $\sim 0.79$  g/cm<sup>3</sup>. As the fluid density is increased to 1 g/cm<sup>3</sup>, the number of molecules participating in hydrogen bonding decreases. This “anomaly” seems to be due, in part, to the restriction that one molecule must be a central molecule, surrounded by a cavity of radius  $r_i$ , empty of any molecular centers.<sup>8,9</sup> That restriction also implies that molecules participating in the hydrogen bonding are not the same (one is the central molecule and the others are its neighbors). Furthermore, if there are molecules in the “cavity” region, there is no reason why they cannot influence the hydrogen bonding. Therefore, it is suggested here that, in evaluating hydrogen bonds, all molecules at  $r(\sigma_f \leq r \leq r_i)$  be considered. This suggestion is in agreement with other authors<sup>16–18</sup> who required in their models that molecules participating in hydrogen bonding be within a given distance from each other, but no cavity restriction was imposed. It should be noted that dropping the requirement for a cavity surrounding the central molecule can eliminate the anomaly noticed earlier. Therefore, the modified expression for the probability that a molecule has  $j$  neighbors in its hydrogen bonding shell would be

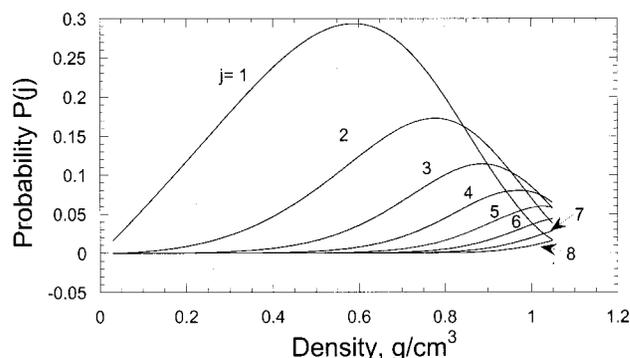


FIG. 8. Probability distribution of finding  $j$  molecules in hydrogen bonding shell.

$$p_j^* = \frac{1}{j!} \left( \frac{24\eta_b}{\sigma_f^3} \int_{\sigma_f}^{r_0} r^2 G(r) dr \right)^j \times \exp \left( - \frac{24\eta_b}{\sigma_f^3} \int_{\sigma_f}^{r_0} r^2 G(r) dr \right). \quad (18)$$

The last expression for  $p_j$  produces better results, as shown by the dotted line in Fig. 7, in which it is shown that the fraction of water molecules participating in hydrogen bonding increases monotonically up to the normal liquid density of 1.0.

(4) It was assumed previously<sup>8,9</sup> that a central molecule will have the maximum possible hydrogen bonding energy if there is only one molecule in its hydrogen bonding shell, and provided that the orientation is favorable. A penalty was assigned to the hydrogen bonding energy, if more than one molecule was in the hydrogen bonding sphere, as noted by the form of Eq. (3). Figure 8 shows the probability distributions for associated water molecules computed using Eq. (11) suggested by Truskett *et al.*<sup>8,9</sup> As the fluid density increases from 0.6 g/cm<sup>3</sup> (for which the probability of having only one neighbor is highest) to 1 g/cm<sup>3</sup>, the probability of finding 2, 3, or 4 molecules increases, as shown in Fig. 8. Therefore, according to the Truskett *et al.* model,<sup>8,9</sup> the hydrogen bonding energy decreases as density is increased from 0.6 to 1 g/cm<sup>3</sup>, whereas in fact it should increase. Another negative consequence of including only one hydrogen bond per water molecule is the following: Confinement reduces the average number of neighbors around a given molecule. This in turn, would cause the disruption of hydrogen bonds, and therefore, decrease the hydrogen bonding energy. But, in fact, if it is assumed that the maximum hydrogen bond energy is attained when 1 or closer to 1 neighbors are in the hydrogen bonding shell of a given molecule, then one could expect that confinement could actually increase the hydrogen bonding energy. This could be one of the reasons for the shift in the wrong direction of the vapor–liquid coexistence curve when the hydrogen bonds were “turned off” (see Fig. 3). On the other hand, water molecules can form up to four hydrogen bonds. To account for this fact, we modified the model for hydrogen bonding as follows. A value of  $\epsilon^{HB}$  was assigned to each hydrogen bond formed. It is assumed that, for  $j$  from 1 to 4, the number of hydrogen bonds is equal to  $j$ .

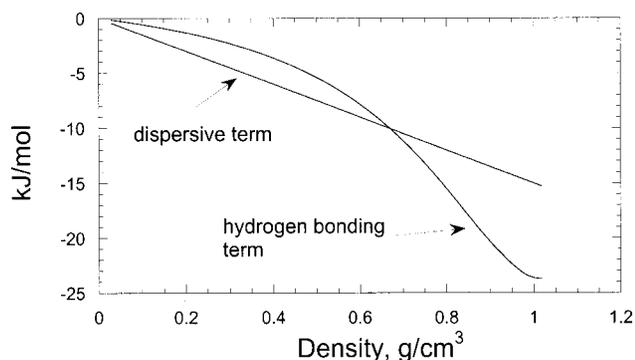


FIG. 9. Contribution of the hydrogen bonding and dispersive interactions to the Helmholtz free energy according to the modified model presented in this work.

Then, for each additional molecule in the hydrogen bonding shell, the number of bonds is decreased by one. It follows that if there are eight or more molecules in the hydrogen bonding shell, that the central molecule is not capable of forming hydrogen bonds at all. With this modification, the Helmholtz free energy expression suggested by Truskett *et al.*<sup>8,9</sup> becomes

$$F = -N\beta^{-1} \left( \ln \left( \frac{1 - \rho_b b_b}{\rho_b \Lambda^3} \right) + 1 \right) - N a_b \rho_b + \frac{N \epsilon^{HB}}{2} \left( \sum_{j=1}^4 j p_j^{\text{bulk}} + \sum_{j=5}^7 (8-j) p_j^{\text{bulk}} \right), \quad (19)$$

where  $p_j^{\text{bulk}}$  is calculated from Eq. (18), and all parameters are the same as in Truskett *et al.*<sup>8</sup>

With these modifications, we recalculated the hydrogen bonding contribution to Helmholtz free energy and compared it with the dispersion term. The results are plotted in Fig. 9.

The results show that these two minor modifications to the original model alter the significance of hydrogen bonding relative to the dispersion term. It seems that it is important that the model accounts for a maximum of four hydrogen bonds per water molecule. A penalty was applied for molecules in excess of four. However, it should be noted that the way we account for four hydrogen bonds ignores the temperature dependence of hydrogen bonds, which has been shown to be crucial for reproducing density anomalies of water.<sup>9</sup> Ongoing efforts are focused on predicting the phase behavior of fluids in porous media considering these modifications to the equation of state for the water-like fluid presented by Truskett *et al.*<sup>8,9</sup>

#### IV. CONCLUSIONS

The equation of state suggested by Truskett *et al.*<sup>8,9</sup> accounts for fluid–fluid, fluid–wall and hydrogen bonding in-

teractions for a confined water-like fluid. The original model<sup>8,9</sup> gives a reasonable and comprehensive description of the phase behavior of bulk and confined water. However, some parameter values used in Refs. 8 and 9 do not appear to be appropriate for describing liquid phase water at 298 K and 1 bar, since some of the predicted results deviate from experimental observations. It also appears that the predicted results are extremely sensitive to some parameter values. It is suggested here that a better alternative to determine those parameters for bulk fluids is to specify the pressures, use the pressure equations for bulk liquid and the vapor phase in equilibrium with it, and use the fact that chemical potentials of these two phases are equal at equilibrium.

Further, it was shown that the simplification of attributing just one hydrogen bonding capability to water can lead to qualitatively wrong results. A model that accounts for four hydrogen bonding was shown to yield more sensible results. The notion of a central molecule is not needed, and may even yield incorrect predictions of fluid parameters.

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