

## A THERMODYNAMIC MODEL OF SUPERCOOLED WATER

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**Summary:** *A thermodynamic model of liquid and amorphous phases of water developed. Water is considered as a mixture of a low density structure (LDS) and a high density structure (HDS). When temperature or pressure are decreased, increasing number of water molecules participate in the LDS, assumed to resemble, on the local scale, the  $I_h$  or  $I_c$  ices. This explains the anomaly in density and heat capacity. Mathematically, the model comprises several algebraic relations containing a number of parameters, determined by fitting the measured thermodynamic properties of stable, supercooled, and superheated water. The model predicts that below approx. 223 K liquid water can exist in two distinct phases. At 77 K, the model predicts the densities of the so-called low density amorphous ice and high density amorphous ice with a good accuracy. On the same basis a model for surface tension of supercooled water was developed, reproducing the observed anomaly near 267°K.*

### 1. Introduction

When cooling water below the freezing temperature (273.16 K) rapidly, it remains liquid for some time in a metastable state. Supercooled water is important in a number of natural phenomena and technological applications, such as droplet formation near airfoils and in the free atmosphere, cryopreservation of food and biological material, geology. In the supercooled region, the anomalous properties of water are magnified. Recently, the present author developed a thermodynamic model of water, which is further elaborated in this contribution.

It is generally assumed and confirmed indirectly by recent experiments (Wölk & Strey 2001, Peeters *et al.* 2002) that the critical clusters of water are liquid-like even far below the triple point temperature 273.15 K. Contemporary accurate empirical formulation of thermodynamic properties of water (Wagner & Pruß 2002, IAPWS 1996) is conditionally valid down to 240 K and relation for surface tension (Vargaftik 1983, IAPWS 1994) is only applicable above 273.15 K. Recently we developed a thermodynamic model (Hrubý & Holten 2004). In the present paper, the outline of the model is given, and the surface thermodynamics is further elaborated. The model is based on the hypothesis that liquid water consists of two structures. At an instant of time, each water molecule participates either in the low-density structure (LDS), or in the high-density structure (HDS). The distribution of molecules between the two structures is given by *structural fraction*  $x$ , given as

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$$x = \frac{N_{\text{HDS}}}{N_{\text{LDS}} + N_{\text{HDS}}} = \frac{\text{number of HDS members}}{\text{total number of molecules}}. \quad (1)$$

## 2. Specific volume

We assume that the mixture is volumetrically ideal. The specific volume is then

$$v(p, T, x) = (1-x)v_{\text{LDS}}(p, T) + xv_{\text{HDS}}(p, T), \quad (2)$$

where  $v_{\text{LDS}}$  and  $v_{\text{HDS}}$  are specific volumes of hypothetical pure structures.

We assume that LDS is similar on the local scale to the ordinary ice *Ih*. Therefore, we approximate  $v_{\text{LDS}} \approx v_{\text{Ih}}$ . Röttger *et al.* (Röttger *et al.* 1994) give lattice constants  $a$  and  $c$  for ordinary and heavy water measured with synchrotron radiation at normal pressure  $p_n=101325$  Pa. These constants can be used to compute volume of a unit cell of the *Ih*-ice lattice as  $V_{\text{uc}} = \frac{1}{2}\sqrt{3a^2c}$ . The lattice contains 4 water molecules per unit cell. Therefore, the specific volume can be obtained as  $v_{\text{Ih}} = V_{\text{uc}}N_{\text{A}} / (4M)$ , where the Avogadro constant is  $N_{\text{A}} = 6.0221367 \times 10^{26} \text{ kmol}^{-1}$  and the molecular masses of ordinary and heavy water are, respectively,  $M_{\text{H}_2\text{O}} = 18.015268 \text{ kg/kmol}$  (Vienna Standard Mean Ocean Water, VSMOW) and  $M_{\text{D}_2\text{O}} = 20.027508 \text{ kg/kmol}$ . The original authors suggested a polynomial fit for the unit cell volume. Transformed to the specific volume as explained above, their formula can be written as

$$v_{\text{Ih},n} = a_1 + a_2T^3 + a_3T^4 + \dots + a_nT^{n+1}, \quad (3)$$

where  $n = 6$  for ordinary water and  $n = 7$  for heavy water. Linear and quadratic terms are left out to ensure that expansivity and its derivative with respect to temperature vanish at absolute zero, as required by theory. Unfortunately, the fit parameters are given with insufficient accuracy by the original authors. The least square fit values obtained by the present author are given in table. The fitting function (3) does not perform well above 150 K where its derivatives become wavy. It is definitely not suitable for extrapolation to higher temperatures where it diverges rapidly. Because extrapolation to higher temperatures is important for the present application, we chose a different functional form, valid down to 0 K and extrapolable to  $T > 273.15$ :

$$v_{\text{Ih},n} = a_1 + a_2t(1-y-ty) + a_3t^2(1-y) + a_4\left(1+t+\frac{1}{2}t^2\right)y + a_5t^3y, \quad (4)$$

where  $t \equiv T/a_6$  and  $y \equiv \exp(-t)$ . The parameters of relations (3) and (4) are given in Table 1.

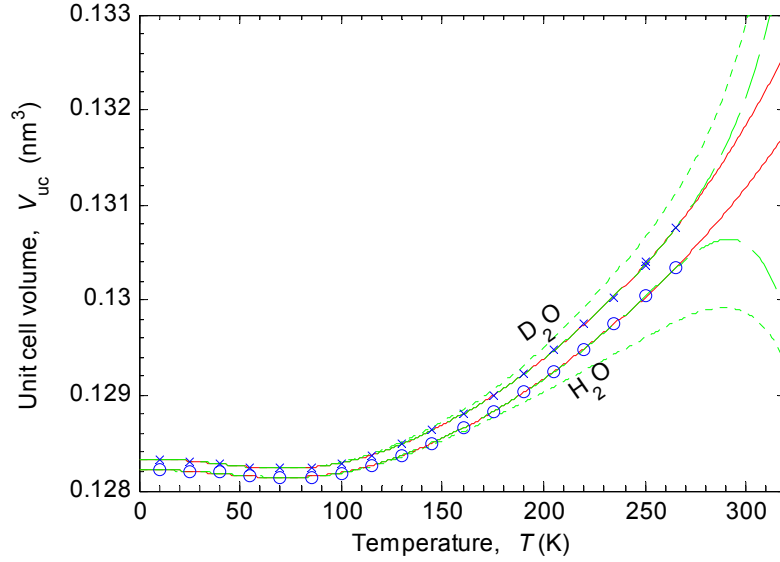
An empirical equation was assumed for the specific volume of the high-density structure (HDS) at normal pressure:

$$v_{\text{HDS},n}/b_1 = 1 + (T/b_2)^{b_3}. \quad (5)$$

Parameters  $b_1$ ,  $b_2$ , and  $b_3$ , are given in Table 2.

**Table 1.** Parameters of relations (3) and (4) for the specific volume of ice Ih. The values are valid for volume in  $\text{m}^3 \text{kg}^{-1}$  and temperature in K.

	H <sub>2</sub> O, Eq. (3)	H <sub>2</sub> O, Eq. (4)	D <sub>2</sub> O, Eq. (3)	D <sub>2</sub> O, Eq. (4)
a <sub>1</sub>	1.07152E-03	1.21779E-03	9.64704E-04	1.23948E-03
a <sub>2</sub>	-1.21450E-11	-4.33629E-05	-1.54036E-11	-8.36598E-05
a <sub>3</sub>	2.34475E-13	4.38031E-06	3.38321E-13	7.97544E-06
a <sub>4</sub>	-1.57309E-15	-1.46258E-04	-2.85927E-15	-2.74776E-04
a <sub>5</sub>	4.70663E-18	-9.88480E-06	1.23816E-17	-1.53547E-05
a <sub>6</sub>	-5.30435E-21	5.58300E+01	-2.74086E-20	5.83500E+01
a <sub>7</sub>			2.46942E-23	



**Figure 1.** Volume of the unit cell of the Ih lattice of ordinary and heavy water. Open circles and crosses: data by Röttger *et al.* (Röttger *et al.* 1994) for ordinary and heavy water, respectively. Solid lines: Eq. (4). Dashed lines: Eq. (3). Dotted lines: Eq. (3) with original (inaccurate) coefficients (Röttger *et al.* 1994)

The water molecules are free to join LDS or HDS. Therefore, the structural fraction  $x$  for given pressure and temperature is obtained by minimizing the Gibbs function with respect to  $x$ . We proposed a simple model

$$g(p, T, x) = g_{\text{LDS}}(T) + h_1(p)x + h_2x + RT[(1-x)\ln(1-x) + x\ln x], \quad (6)$$

where

$$h_1 = h_{1n} + (p - p_n)(v_{\text{HDS},n} - v_{\text{LDS},n}). \quad (7)$$

The last condition neglects compressibility of the pure structures.

Conditions for a local minimum of the Gibbs function are

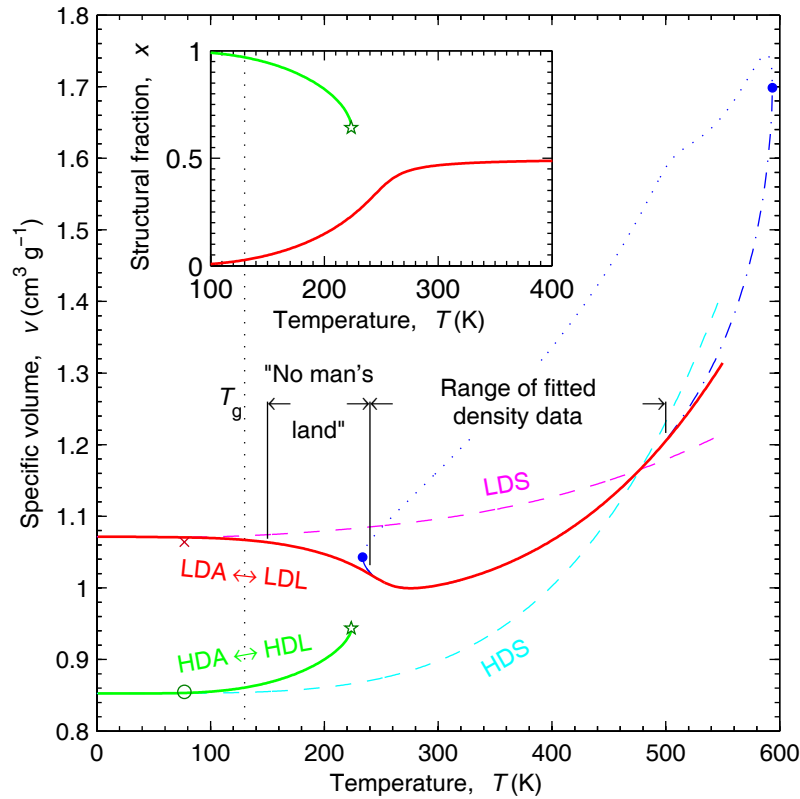
$$g_x = 0, \quad g_{xx} > 0. \quad (8)$$

Subscript “x” denotes a derivative with respect to  $x$  at constant  $p$  and  $T$ ; double “xx” denotes second derivative. Condition (8) was applied to the Gibbs function (6). The solution can be found by iterating equation

$$x_\Phi = \frac{1}{1 + \exp\left[\frac{(h_1 + 2x_\Phi h_2)}{T}\right]}, \quad (9)$$

starting from  $x = 0$  for  $\Phi = \text{LDA/LDL}$  and  $x = 1$  for  $\Phi = \text{HDA/HDL}$ .

Parameters  $b_1, b_2, b_3, h_{1n},$  and  $h_2$  have been obtained by fitting liquid densities (Wagner & Pruß 2002) in the range 240—500 K. Values of the parameters are given in Table 2. Results are shown at Figure 2. At  $p_n$  below 223 K the model predicts two liquid phases, the more stable (higher  $g$ ) low-density liquid (LDL) and the high-density liquid (HDL). It is assumed that they transform into the low-density amorphous ice (LDA) and high-density amorphous ice (HDA), respectively, at glass temperature  $T_g \approx 130$  K. Interestingly, the experimental densities of LDA (cross) and HDA (open circle) at 77 K are predicted accurately.



**Figure 2.** Specific volume of ordinary water at normal pressure. Solid lines: liquid and amorphous phases predicted by the present model. Dashed lines: pure low-density and high-density structures. Star: liquid-liquid (HDL-LDL) spinodal point predicted by the present model. Dashed-dotted line: IAPWS-95 (IAPWS 1996), stable solution. Dotted line: unstable

solution. Solid circles: liquid-vapor spinodal points (IAPWS 1996).  $T_g$ : glass transition temperature. Inset: structural fraction for the liquid and amorphous phases.

### 3. Heat capacity at constant pressure

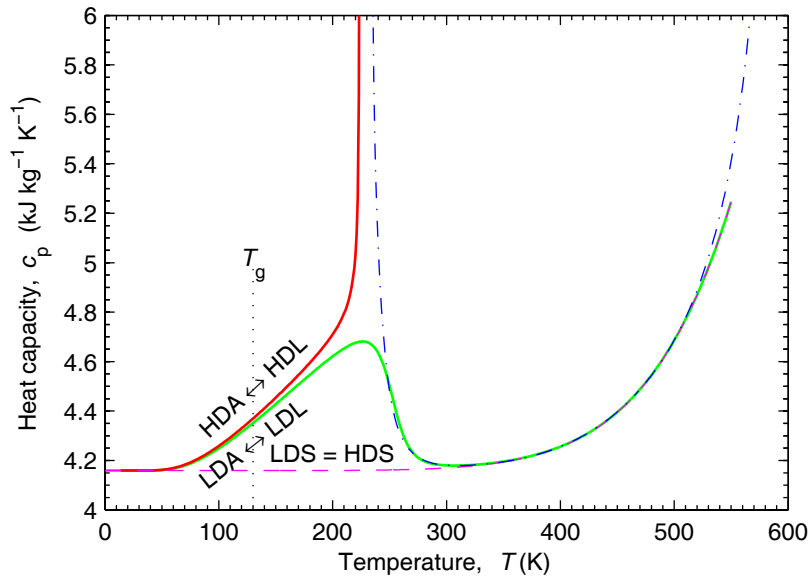
Following equation (6), heat capacity at constant pressure is given as

$$c_{p,\Phi} = c_{p,LDS}(T) + \frac{RT \ln^2 \frac{x_\Phi}{1-x_\Phi}}{2h_2 + T \left( \frac{1}{1-x_\Phi} + \frac{1}{x_\Phi} \right)}. \quad (10)$$

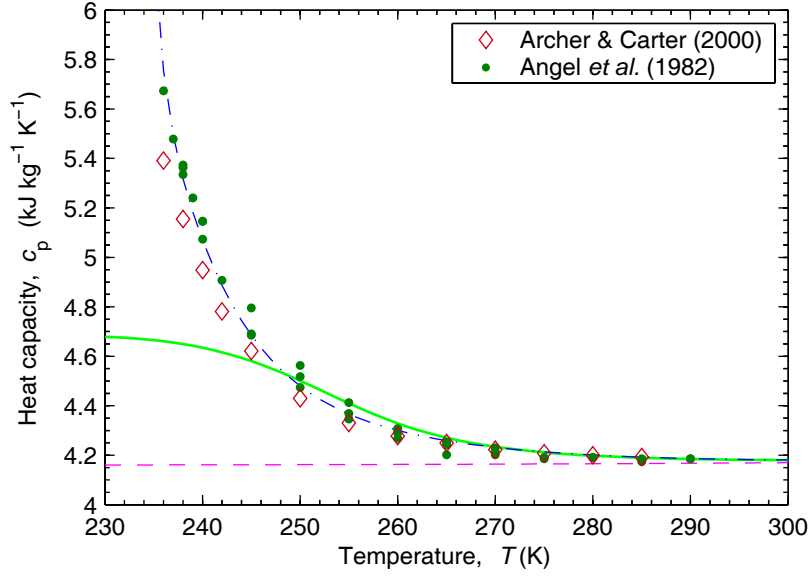
The second term gives rise to the anomalous increase of heat capacity of supercooled water when temperature is decreased. The first term is related to the function  $g_{LDS}(T)$  and we assume it in the form

$$c_{p,LDS} = T \frac{\partial s_{LDS}}{\partial T} = -T \frac{\partial^2 g_{LDS}}{\partial T^2} = R d_1 \left[ 1 + \left( \frac{T}{d_2} \right)^{d_3} \right]. \quad (11)$$

The coefficients  $d_1$ ,  $d_2$ , and  $d_3$  were obtained by fitting heat capacity obtained from the IAPWS-95 formulation (Wagner & Pruß 2002) in high temperature range (276-500K). Below the triple point,  $c_{p,LDS}$  is almost constant, giving just an offset to the anomalous part. The heat capacities are plotted in Figure 3 and Figure 4.



**Figure 3.** Constant-pressure heat capacity of liquid phases of water. Below the glass temperature  $T_g$ , heat capacity is substantially decreased (ignored in this figure). Solid lines: prediction of the present model. Dashed line: heat capacity of pure low-density structure (equal to that of pure high-density structure). Dash-dotted line: IAPWS-95 formulation (IAPWS 1996).



**Figure 4.** Constant-pressure heat capacity of supercooled water at normal pressure. A detail showing existing experimental data.

As shown at Figure 4, the model is in agreement with heat capacity experimental data only down to about 245 K. Below this temperature, the anomalous increase is underpredicted.

#### 4. Gibbs free energy and pressure of saturated vapor

Function  $g_{\text{LDS}}(T)$  was obtained by integrating equation (11) twice:

$$g_{\text{LDS}}(T) = R \left\{ -d_1 T \left[ \ln T - 1 + \frac{1}{d_3(d_3 + 1)} \left( \frac{T}{d_2} \right)^{d_3} \right] - d_4 T + d_5 \right\}. \quad (12)$$

The two integration constants  $c_4$  and  $c_5$  were determined such that the entropy and internal energy of liquid water at triple point are equal to zero. This is the reference state choice of the IAPWS-95 formulation (Wagner & Pruß 2002).

**Table 2.** Parameters of relations (5), (6), (12), (17), (18).

$h_{1n}$	K	493.99	$b_1$	$\text{m}^3\text{kg}^{-1}$	8.5266e-4
$h_2$	K	-486.47	$b_2$	K	607.66
$d_1$	1	9.0117	$b_3$	1	4.1571
$d_2$	K	655.97	$\mathbf{P}_{\text{LDS}}$	1	52.9316
$d_3$	1	7.613	$\mathbf{P}_{\text{HDS}}$	1	39.4034
$d_4$	1	-51.2435	$n$	1	4.511
$d_5$	K	-2584.94	$c_1$	$\text{N m}^{-1}$	1e-3
$R$	$\text{J kg}^{-1} \text{K}^{-1}$	461.51805	$c_2$	$\text{kg m}^{-3}$	18015.268

The pressure of saturated vapor was computed by equating the Gibbs free energy of the liquid, either LDL or HDL, and the Gibbs free energy of the vapor

$$g_{\Phi}(p_{\text{sat},\Phi}, T) = g_{\text{vapor}}(p_{\text{sat},\Phi}, T). \quad (13)$$

Here the liquid was computed using the present model, represented by equations (6) and (12). The Gibbs free energy of the water vapor was computed assuming ideal gas behavior and the ideal gas Gibbs free energy at  $p_n$  given by IAPWS-95 (Wagner & Pruß 2002):

$$g_{\text{vapor}}(p_{\text{sat},\Phi}, T) = g_{\text{vapor},n}(T) + RT \ln \frac{p_{\text{sat},\Phi}}{p_n}. \quad (14)$$

Saturated vapor pressure can be computed by iterating the following equation, starting from  $p_{\text{sat},\Phi} = 0$ :

$$p_{\text{sat},\Phi} = p_n \exp \frac{(p_n - p_t)v_{\Phi_{\text{nt}}} + (p_{\text{sat},\Phi} - p_n)v_{\Phi_n} + g_{\Phi_n} - g_{\Phi_{\text{nt}}} - RT_t \ln \frac{p_n}{p_t} - g_{\text{Gn}} + g_{\text{Gnt}}}{RT}. \quad (15)$$

Here the triple-point temperature and pressure are, respectively,  $T_t = 273.16$  K and  $p_t = 611.655$  Pa. Further,  $v_{\Phi_n}$  and  $v_{\Phi_{\text{nt}}}$  are specific volumes of the given liquid phase  $\Phi$  (LDL or HDL below 223 K) at normal pressure and, respectively, at the actual temperature and triple-point temperature;  $g_{\Phi_{\text{nt}}}$  and  $g_{\Phi_n}$  are Gibbs energies of the given liquid phase  $\Phi$  given by Eq. (6) at normal pressure and, respectively, the actual temperature and triple-point temperature;  $g_{\text{Gn}}$  and  $g_{\text{Gnt}}$  are Gibbs energies of gaseous phase (vapor) at normal pressure and, respectively, the actual temperature and triple-point temperature, computed from the IAPWS-95 formulation

$$\frac{g_{\text{Gn}}}{RT} = 1 + \ln \delta + n_1^{\circ} + n_2^{\circ} \tau + n_3^{\circ} \ln \tau + \sum_{i=4}^8 n_i^{\circ} \ln [1 - \exp(-\gamma_i^{\circ} \tau)], \quad (16)$$

where the coefficients  $n_i^{\circ}$  and exponents  $\gamma_i^{\circ}$  are taken from Table 6.1 of Ref. (Wagner & Pruß 2002),  $\tau = T_c / T$ , and  $\delta = \rho / \rho_c$ . The critical temperature and density for water are, respectively,  $T_c = 647.096$  K and  $\rho_c = 322$  kg m<sup>-3</sup> (Wagner & Pruß 2002). On the contrary to the full IAPWS-95, the ideal gas equation (16) is valid for arbitrarily low temperatures.

Within the range of validity of the IAPWS-95 formulation (down to about 240 K), the vapor pressures computed using Eq. (15) are in a very good agreement with the vapor pressures computed from the IAPWS-95.

## 5. Surface tension and adsorption (surface density enrichment)

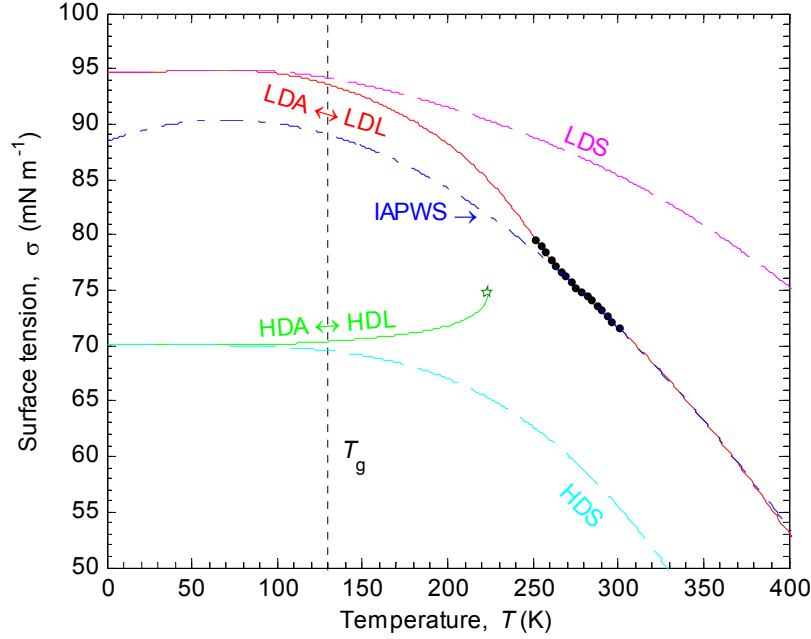
Considering liquid water as mixture of “components” LDS and HDS, the surface tension can be described with the Macleod-Sugden correlation (Poling *et al.* 2001):

$$\sigma(T, x)/c_1 = [\mathbf{P}(x)/c_2 v(T, x)]^n. \quad (17)$$

Here,  $c_1$  and  $c_2$  are constants ensuring dimensional consistency,  $\mathbf{P}$  is the *parachor*:

$$\mathbf{P}(x) = (1-x)\mathbf{P}_{\text{LDS}} + x\mathbf{P}_{\text{HDS}}. \quad (18)$$

The pure-component parachors  $\mathbf{P}_{\text{LDS}}$  and  $\mathbf{P}_{\text{HDS}}$ , and the exponent  $n$ , were found by fitting surface tension data by Hacker (Hacker 1951) for 251—273 K and IAPWS (IAPWS 1994) for 273—373 K. The results in an extended temperature range are shown at Figure 5.



**Figure 5.** Surface tension of liquid and amorphous phases of water. Solid lines: Eq.(17). Dots: Experimental data by Hacker (Hacker 1951).

The adsorptions (surface excesses) of both components can be defined as

$$\Gamma_i = \int_0^\infty [\rho_i(z) - \rho_i^\infty] dz, \quad i = \text{LDS, HDS}, \quad (19)$$

where  $\rho_{\text{LDS}} = (1-x)/v$  and  $\rho_{\text{HDS}} = x/v$ . If Eq. (2) is valid also in the surface layer, the adsorptions (19) are related as

$$\sum_i \Gamma_i v_i = \Gamma_{\text{HDS}} v_{\text{HDS}} + \Gamma_{\text{LDS}} v_{\text{LDS}} = 0. \quad (20)$$

In the Gibbs adsorption equation we expand the differentials of chemical potentials:

$$d\sigma = -\sum_i \Gamma_i d\mu_i = -\left(\sum_i \Gamma_i \mu_{i,x}\right) dx - \left(\sum_i \Gamma_i v_i\right) dp. \quad (21)$$

Owing to Eq. (20), surface tension is independent of pressure and

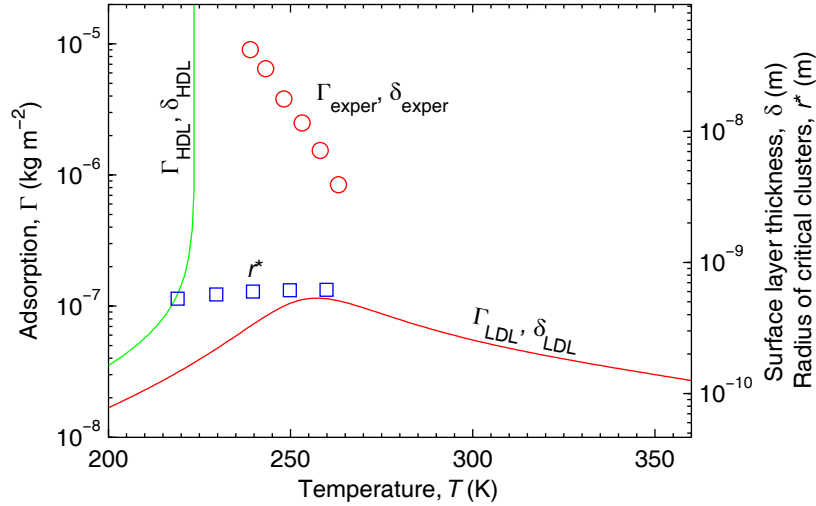
$$\sigma_x = -\sum_i \Gamma_i \mu_{i,x}. \quad (22)$$



Further we compute the chemical potentials and their derivatives:

$$\mu_{\text{LDS}} = g - x g_x, \quad \mu_{\text{HDS}} = g + (1-x) g_x, \quad \mu_{\text{LDS},x} = -x g_{xx}, \quad \mu_{\text{HDS},x} = (1-x) g_{xx}. \quad (23)$$

Solving equations (20) and (22) we have



**Figure 6.** Adsorption (surface excess), surface layer thickness, and size of critical cluster.

$$\Gamma_{\text{LDS}} = \frac{\sigma_x v_{\text{HDS}}}{g_{xx} v}, \quad \Gamma_{\text{HDS}} = -\frac{\sigma_x v_{\text{LDS}}}{g_{xx} v}, \quad \Gamma = \Gamma_{\text{LDS}} + \Gamma_{\text{HDS}} = \frac{\sigma_x (v_{\text{HDS}} - v_{\text{LDS}})}{g_{xx} v}. \quad (24)$$

The “total adsorption”  $\Gamma$ , the surface enrichment irrespective to the membership of molecules, can be compared (see Figure 6) with data deduced from density measurements by Hare and Sorensen (Hare & Sorensen 1987). If this data is correct, the present model underestimates the surface excess by at least one order of magnitude. Also shown is the surface layer thickness  $\delta = \Gamma / \Delta\rho$ ,  $\Delta\rho \equiv \rho(0) - \rho(\infty) \approx \rho_{\text{HDS}} - \rho_{\text{LDS}} = 215.3 \text{ kg m}^{-3}$  (at 273.15 K). The thickness  $\delta$  can be compared with the critical cluster size  $r^*$  by Wölk and Strey (Wölk & Strey 2001). We see that  $r^*$  is of similar magnitude as  $\delta$  or even  $r^* \ll \delta$  (in comparison with).

## 6. Conclusions

A thermodynamic model was developed, enabling a plausible extrapolation of thermodynamic properties of water deep into the supercooled region. Below 223 K, the model predicts existence of a second, denser, liquid phase. This behavior is in accord with hypotheses given in literature (Mishima & Stanley 1998). Further, the model predicts that there is a surface layer of higher density on water surface. Qualitatively, this prediction is in accord with experimental observations (Hare & Sorensen 1987). We conclude that the properties of the critical cluster in homogeneous nucleation are probably similar to the properties of the surface layer and quite dissimilar to the properties of bulk liquid water.

## 7. Acknowledgments

This work was supported by Grant No. 101/03/Z031 GA CR. Some computations and literature search were done by Vincent Holten of the Eindhoven University of Technology, Dept. Applied Physics.

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