Supporting Information

Deriving the fraction of molecules involved at least once in self-association

Alcohols are commonly modeled within the SAFT framework with two or three association sites. A clear basis for the choice of alcohols association scheme does not seem to exist in the literature. As a result, we examine the effect of association scheme on the fraction of molecules involved at least once in self-association. In other words, we examine the fraction of alcohol molecules that are bonded at least once to another alcohol molecule and the fraction of water molecules that are bonded at least once to another water molecule. Results using a two site alcohol model 2(1,1) and a three site alcohol model 3(2,1) are compared with simulation to decide on the best choice of association scheme for modeling alcohol + water binary systems.

For the case of a **two site alcohol model**, A and B, represent the hydrogen and the oxygen atom respectively. Water is modeled as a hard sphere with four association sites, where two of them (A and B) stand for the hydrogen atoms and the others (C and D) represent the oxygen atoms. In the framework of Wertheim's multi-density formalism, the contributions due to associations are:

$$\frac{\Delta c^{(o)}}{V} = \frac{\Delta c^{(ww)}}{V} + \frac{\Delta c^{(wa)}}{V} + \frac{\Delta c^{(aa)}}{V} \tag{1}$$

Where $\frac{\Delta c^{(ww)}}{V}$, $\frac{\Delta c^{(wa)}}{V}$, and $\frac{\Delta c^{(aa)}}{V}$ are the water-water, water-alcohol, and alcohol-alcohol association contributions, respectively. Following SAFT and Wertheim's first order thermodynamic perturbation theory, each contribution is written as:

$$\frac{\Delta c^{(ww)}}{V} = \left(\sigma^{w}_{\Gamma-A}\sigma^{w}_{\Gamma-B} + \sigma^{w}_{\Gamma-A}\sigma^{w}_{\Gamma-C} + \sigma^{w}_{\Gamma-D}\sigma^{w}_{\Gamma-B} + \sigma^{w}_{\Gamma-D}\sigma^{w}_{\Gamma-C}\right)\Delta_{ww} \tag{2}$$

$$\frac{\Delta c^{(wa)}}{V} = \left(\sigma^{w}_{\Gamma-A} \sigma^{a}_{\Gamma-B} + \sigma^{w}_{\Gamma-B} \sigma^{a}_{\Gamma-A} + \sigma^{w}_{\Gamma-C} \sigma^{a}_{\Gamma-A} + \sigma^{w}_{\Gamma-D} \sigma^{a}_{\Gamma-B} \right) \Delta_{wm} \tag{3}$$

$$\frac{\Delta c^{(aa)}}{V} = \left(\sigma^{a}_{\Gamma-A} \sigma^{a}_{\Gamma-B} \right) \Delta_{aa} \tag{4}$$

Where in theses equation, the term $\sigma^{w}_{\Gamma-A}$ is the density of water molecules which are not bonded at site A, and Δ_{ww} is the association strength between two bonded water molecules. Similar definitions apply for $\sigma^{w}_{\Gamma-B}, \sigma^{w}_{\Gamma-C}, \sigma^{w}_{\Gamma-D}, \sigma^{a}_{\Gamma-A}, \sigma^{a}_{\Gamma-B}, \Delta_{wa}, \Delta_{aa}$.

The total alcohol number density is calculated as:

$$\rho_a = \rho_{o_a} + \rho_{A_a} + \rho_{B_a} + \rho_{AB_a} \tag{5}$$

Where, ρ_{o_a} is the density of alcohol molecules not bonded to any other molecules, ρ_{A_a} is the density of alcohol molecules bonded at site A, and ρ_{AB_a} is the density of alcohol molecules bonded at both sites A and B.

According to Wertheim's theory, one can easily obtain the density of water/alcohol in different bonding states using the graphical derivatives of the association contribution:

$$\frac{\rho^{(aa)}_{A_a}}{\rho_{o_a}} = \frac{\partial \Delta c^{(aa)} / V}{\partial \sigma^{a}_{\Gamma-A}} = \left(\sigma^{a}_{\Gamma-B} \right) \Delta_{wa} \tag{6}$$

$$\frac{\rho^{(aa)}_{B_a}}{\rho_{o_a}} = \frac{\partial \Delta c^{(aa)} / V}{\partial \sigma^{a}_{\Gamma-B}} = \left(\sigma^{a}_{\Gamma-A} \right) \Delta_{wm} \tag{7}$$

Where $\rho_{A_a}^{(aa)}$ is the density of alcohol molecules with **only** site A bonded to another alcohol molecule. The density of alcohol molecules that are bonded at both sites (A and B):

$$\rho_{AB_a} = \rho_{AB_a}^{(waw)} + \rho_{AB_a}^{(waa)} + \rho_{AB_a}^{(waa)} \tag{8}$$

Where $\rho_{AB_a}^{(waw)}$ is the density of alcohol molecules that are bonded to a water molecule at each site (A and B). The other two terms are defined in an identical way. In this work, since only the density of alcohol molecules that are bonded at least once to another alcohol molecule is needed, we have:

$$\frac{\rho_{AB_m}}{\rho_{o_m}} = c_{A_m} c_{B_a} = \frac{\partial \Delta c^{(o)}/V}{\partial \sigma^a_{\Gamma-A}} * \frac{\partial \Delta c^{(o)}/V}{\partial \sigma^a_{\Gamma-B}} = \left(\frac{\partial \Delta c^{(wa)}/V}{\partial \sigma^a_{\Gamma-A}} + \frac{\partial \Delta c^{(aa)}/V}{\partial \sigma^a_{\Gamma-A}} \right) * \left(\frac{\partial \Delta c^{(wa)}/V}{\partial \sigma^a_{\Gamma-A}} + \frac{\partial \Delta c^{(aa)}/V}{\partial \sigma^a_{\Gamma-A}} \right) \tag{9}$$

$$\frac{\rho_{AB_a}^{(waa)}}{\rho_{o_a}} = \frac{\partial \Delta c^{(wa)}/V}{\partial \sigma^a_{\Gamma-A}} * \frac{\partial \Delta c^{(aa)}/V}{\partial \sigma^a_{\Gamma-B}} + \frac{\partial \Delta c^{(aa)}/V}{\partial \sigma^a_{\Gamma-A}} * \frac{\partial \Delta c^{(wa)}/V}{\partial \sigma^a_{\Gamma-B}} \tag{10}$$

$$\frac{\rho_{AB_a}^{(waa)}}{\rho_{o_a}} = \left(\sigma^w_{\Gamma-B} + \sigma^w_{\Gamma-C} \right) \Delta_{wa} * \left(\sigma^a_{\Gamma-A} \right) \Delta_{aa} + \left(\sigma^a_{\Gamma-B} \right) \Delta_{aa} * \left(\sigma^w_{\Gamma-A} + \sigma^w_{\Gamma-D} \right) \Delta_{wa} \tag{11}$$

$$\frac{\rho_{AB_a}^{(aaa)}}{\rho_{o_a}} = \frac{\partial \Delta c^{(aa)}/V}{\partial \sigma^a_{\Gamma-A}} * \frac{\partial \Delta c^{(aa)}/V}{\partial \sigma^a_{\Gamma-B}} \tag{12}$$

$$\frac{\rho_{AB_a}^{(aaa)}}{\rho_{o_a}} = \left(\sigma^a_{\Gamma-B} \right) \Delta_{aa} * \left(\sigma^a_{\Gamma-A} \right) \Delta_{aa} \tag{13}$$

So, the fraction of alcohol molecules bonded at least once to another alcohol molecule is:

$$\frac{\rho_a^{(aa)}}{\rho_a} = \frac{\rho_{A_a}^{(aa)}}{\rho_a} + \frac{\rho_{B_a}^{(aa)}}{\rho_a} + \frac{\rho_{AB_a}^{(waa)}}{\rho_a} + \frac{\rho_{AB_a}^{(aaa)}}{\rho_a} \tag{14}$$

Extending each term in details:

$$\frac{\rho_a^{(aa)}}{\rho_a} = X_{o_a}\left(\sigma^a_{\Gamma-B}\right)\Delta_{wa} + X_{o_a}\left(\sigma^a_{\Gamma-A}\right)\Delta_{wa} + X_{o_a}\left(\sigma^w_{\Gamma-B} + \sigma^w_{\Gamma-C}\right)\Delta_{wa} * \left(\sigma^a_{\Gamma-A}\right)\Delta_{aa} \\ + X_{o_a}\left(\sigma^a_{\Gamma-B}\right)\Delta_{aa} * \left(\sigma^a_{\Gamma-A} + \sigma^w_{\Gamma-D}\right)\Delta_{wa} + X_{o_a}\left(\sigma^a_{\Gamma-B}\right)\Delta_{aa} * \left(\sigma^a_{\Gamma-A}\right)\Delta_{aa} \quad (15)$$

Defining the fraction of alcohol molecules not bonded at site A as: $X_{A_m} = \sigma_{\Gamma-A_m} / \rho_m$, the equation above becomes:

$$\frac{\rho_a^{(aa)}}{\rho_a} = X_{o_a}\left(\rho_a X_{B_a}\right)\Delta_{wa} + X_{o_a}\left(\rho_a X_{A_a}\right)\Delta_{wa} + X_{o_a}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{aa} \\ + X_{o_a}\left(\rho_a X_{B_a}\right)\Delta_{aa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{wa} + X_{o_a}\left(\rho_a X_{B_a}\right)\Delta_{aa} * \left(\rho_a X_{A_a}\right)\Delta_{aa} \quad (16)$$

For the case of a **three site alcohol model**, A, B and C represent the hydrogen atom and the two oxygen atoms, respectively. Water is still modeled as a hard sphere with four association sites, where two of them (A and D) stand for the hydrogen atoms and the others (B and C) represent the oxygen atoms.

Extending the derivation to density states of three-time bonded alcohol:

$$\rho_{ABC_a} = \rho^{(wwaw)}_{ABC_a} + \rho^{(wwaa)}_{ABC_a} + \rho^{(waaa)}_{ABC_a} + \rho^{(aaaa)}_{ABC_a} \quad (17)$$

$$\frac{\rho_{AB_a}}{\rho_{o_a}} = c_{A_a} c_{B_a} c_{C_a} = \frac{\partial \Delta c^{(o)}/V}{\partial \sigma_{\Gamma-A_a}} * \frac{\partial \Delta c^{(o)}/V}{\partial \sigma_{\Gamma-B_a}} * \frac{\partial \Delta c^{(o)}/V}{\partial \sigma_{\Gamma-C_a}} = \\ \left(\frac{\partial \Delta c^{(wa)}/V}{\partial \sigma_{\Gamma-A_a}} + \frac{\partial \Delta c^{(aa)}/V}{\partial \sigma_{\Gamma-A_a}}\right) * \left(\frac{\partial \Delta c^{(wa)}/V}{\partial \sigma_{\Gamma-B_a}} + \frac{\partial \Delta c^{(aa)}/V}{\partial \sigma_{\Gamma-B_a}}\right) * \left(\frac{\partial \Delta c^{(wa)}/V}{\partial \sigma_{\Gamma-C_a}} + \frac{\partial \Delta c^{(aa)}/V}{\partial \sigma_{\Gamma-C_a}}\right) \quad (18)$$

$$\frac{\rho_{ABC_a}^{(wwaa)}}{\rho_a} = X_{o_a}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{aa} +$$
$$X_{o_a}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{aa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{wa} + \quad (19)$$
$$X_{o_a}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{aa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{wa}$$

$$\frac{\rho_{ABC_a}^{(waaa)}}{\rho_a} = X_{o_a}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{aa} * \left(\rho_a X_{A_a}\right)\Delta_{aa} +$$
$$X_{o_a}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{aa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{aa} + \quad (20)$$
$$X_{o_a}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{aa} * \left(\rho_a X_{A_a}\right)\Delta_{aa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{wa}$$

$$\frac{\rho_{ABC_a}^{(aaaa)}}{\rho_a} = X_{o_a}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{aa} * \left(\rho_a X_{A_a}\right)\Delta_{aa} * \left(\rho_a X_{A_a}\right)\Delta_{aa} \quad (21)$$

So, the fraction of alcohol molecules in each bonding state is calculated as:

$$\frac{\rho_a^{(aa)}}{\rho_a} = \frac{\rho_{A_a}^{(aa)}}{\rho_a} + \frac{\rho_{B_a}^{(aa)}}{\rho_a} + \frac{\rho_{AB_a}^{(waa)}}{\rho_a} + \frac{\rho_{AB_a}^{(aaa)}}{\rho_a} + \frac{\rho_{AC_a}^{(waa)}}{\rho_a} + \frac{\rho_{AC_a}^{(aaa)}}{\rho_a} + \frac{\rho_{BC_a}^{(waa)}}{\rho_a} + \frac{\rho_{BC_a}^{(aaa)}}{\rho_a} + \frac{\rho_{ABC_a}^{(wwaa)}}{\rho_a} + \frac{\rho_{ABC_a}^{(waaa)}}{\rho_a} + \frac{\rho_{ABC_a}^{(aaaa)}}{\rho_a} \quad (22)$$

Performing a similar derivation for water:

$$\rho_w = \rho_{o_w} + \rho_{A_w} + \rho_{B_w} + \rho_{C_w} + \rho_{D_w} + \rho_{AB_w} + \rho_{AC_w} + \rho_{AD_w} + \rho_{BC_w}$$
$$+ \rho_{BD_w} + \rho_{CD_w} + \rho_{ABC_w} + \rho_{ABD_w} + \rho_{BCD_w} + \rho_{ACD_w} + \rho_{ABCD_w} \quad (23)$$

The fraction of water molecules in different bonding states is:

$$\frac{\rho_w^{(ww)}}{\rho_w} = \frac{\rho_{A_w}^{(ww)}}{\rho_w} + \frac{\rho_{B_w}^{(ww)}}{\rho_w} + \frac{\rho_{C_w}^{(ww)}}{\rho_w} + \frac{\rho_{D_w}^{(ww)}}{\rho_w} + \frac{\rho_{AB_w}^{(wwa)}}{\rho_w} + \frac{\rho_{AB_w}^{(www)}}{\rho_w} + \frac{\rho_{AC_w}^{(wwa)}}{\rho_w} + \frac{\rho_{AC_w}^{(www)}}{\rho_w} + \frac{\rho_{AD_w}^{(wwa)}}{\rho_w} + \frac{\rho_{AD_w}^{(www)}}{\rho_w}$$
$$+ \frac{\rho_{BC_w}^{(wwa)}}{\rho_w} + \frac{\rho_{BC_w}^{(www)}}{\rho_w} + \frac{\rho_{BD_w}^{(wwa)}}{\rho_w} + \frac{\rho_{BD_w}^{(www)}}{\rho_w} + \frac{\rho_{CD_w}^{(wwa)}}{\rho_w} + \frac{\rho_{CD_w}^{(www)}}{\rho_w} + \frac{\rho_{ABC_w}^{(wwaa)}}{\rho_w} + \frac{\rho_{ABC_w}^{(wwwa)}}{\rho_w} + \frac{\rho_{ABC_w}^{(wwww)}}{\rho_w}$$
$$+ \frac{\rho_{ABD_w}^{(wwaa)}}{\rho_w} + \frac{\rho_{ABD_w}^{(wwwa)}}{\rho_w} + \frac{\rho_{ABD_w}^{(wwww)}}{\rho_w} + \frac{\rho_{ACD_w}^{(wwaa)}}{\rho_w} + \frac{\rho_{ACD_w}^{(wwwa)}}{\rho_w} + \frac{\rho_{ACD_w}^{(wwww)}}{\rho_w} + \frac{\rho_{BCD_w}^{(wwaa)}}{\rho_w} + \frac{\rho_{BCD_w}^{(wwwa)}}{\rho_w} + \frac{\rho_{BCD_w}^{(wwww)}}{\rho_w} +$$
$$+ \frac{\rho_{ABCD_w}^{(wwwww)}}{\rho_w} + \frac{\rho_{ABCD_w}^{(wwwwa)}}{\rho_w} + \frac{\rho_{ABCD_w}^{(wwwaa)}}{\rho_w} + \frac{\rho_{ABCD_w}^{(wwaaa)}}{\rho_w} \tag{24}$$

Elaborating on each term using the derivatives of the contributions:

$$\frac{\rho_{A_w}^{(ww)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \tag{25}$$

$$\frac{\rho_{B_w}^{(ww)}}{\rho_w} = X_{o_w}\left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} \tag{26}$$

$$\frac{\rho_{C_w}^{(ww)}}{\rho_w} = X_{o_w}\left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} \tag{27}$$

$$\frac{\rho_{D_w}^{(ww)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \tag{28}$$

$$\frac{\rho_{AB_w}^{(wwa)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} + X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} \tag{29}$$

$$\frac{\rho_{AB_w}^{(www)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} \tag{30}$$

$$\frac{\rho_{AC_w}^{(wwa)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} + X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} \quad (31)$$

$$\frac{\rho_{AC_w}^{(www)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} \quad (32)$$

$$\frac{\rho_{AD_w}^{(wwa)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} + X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \quad (33)$$

$$\frac{\rho_{AD_w}^{(www)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \quad (34)$$

$$\frac{\rho_{BC_w}^{(wwa)}}{\rho_w} = X_{o_w}\left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} + X_{o_w}\left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{A_w}\right)\Delta_{ww} \quad (35)$$

$$\frac{\rho_{BC_w}^{(www)}}{\rho_w} = X_{o_w}\left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} \quad (36)$$

$$\frac{\rho_{BD_w}^{(wwa)}}{\rho_w} = X_{o_w}\left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} + X_{o_w}\left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \quad (37)$$

$$\frac{\rho_{BD_w}^{(www)}}{\rho_w} = X_{o_w}\left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \quad (38)$$

$$\frac{\rho_{CD_w}^{(wwa)}}{\rho_w} = X_{o_w}\left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} + X_{o_w}\left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \quad (39)$$

$$\frac{\rho_{CD_w}^{(www)}}{\rho_w} = X_{o_w}\left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \quad (40)$$

$$\frac{\rho_{ABC_w}^{(wwww)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} \tag{41}$$

$$\begin{aligned}\frac{\rho_{ABC_w}^{(wwwa)}}{\rho_w} = {} & X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} + \\ & X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} + \\ & X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww}\end{aligned} \tag{42}$$

$$\begin{aligned}\frac{\rho_{ABC_w}^{(wwaa)}}{\rho_w} = {} & X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} + \\ & X_{o_w}\left(\rho_m X_{B_m}\right)\Delta_{wm} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} + \\ & X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww}\end{aligned} \tag{43}$$

$$\frac{\rho_{ABD_w}^{(wwww)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \tag{44}$$

$$\begin{aligned}\frac{\rho_{ABD_w}^{(wwwa)}}{\rho_w} = {} & X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} + \\ & X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} + \\ & X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}\end{aligned} \tag{45}$$

$$\begin{aligned}\frac{\rho_{ABD_w}^{(wwaa)}}{\rho_w} = {} & X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} + \\ & X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} + \\ & X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}\end{aligned} \tag{46}$$

$$\frac{\rho_{ACD_w}^{(wwww)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \tag{47}$$

$$\frac{\rho_{ACD_w}^{(wwwa)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} +$$
$$X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} + \quad (48)$$
$$X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}$$

$$\frac{\rho_{ACD_w}^{(wwaa)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} +$$
$$X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} + \quad (49)$$
$$X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}$$

$$\frac{\rho_{DBC_w}^{(wwww)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} \quad (50)$$

$$\frac{\rho_{DBC_w}^{(wwwa)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} +$$
$$X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} + \quad (51)$$
$$X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww}$$

$$\frac{\rho_{DBC_w}^{(wwaa)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} +$$
$$X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} + \quad (52)$$
$$X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww}$$

$$\frac{\rho_{ABCD_w}^{(wwwww)}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww}$$
$$* \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \quad (53)$$

$$\frac{\rho^{(wwwwa)}_{ABCD_w}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa}$$
$$+ X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}$$
$$+ X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}$$
$$+ X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} \quad (54)$$

$$\frac{\rho^{(wwwaa)}_{ABCD_w}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa}$$
$$+ X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}$$
$$+ X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}$$
$$+ X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}$$
$$+ X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa}$$
$$+ X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} \quad (55)$$

$$\frac{\rho^{(wwaaa)}_{ABCD_w}}{\rho_w} = X_{o_w}\left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa}$$
$$+ X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}$$
$$+ X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_w X_{B_w} + \rho_w X_{C_w}\right)\Delta_{ww}$$
$$+ X_{o_w}\left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} * \left(\rho_w X_{A_w} + \rho_w X_{D_w}\right)\Delta_{ww} * \left(\rho_a X_{A_a}\right)\Delta_{wa} * \left(\rho_a X_{B_a} + \rho_a X_{C_a}\right)\Delta_{wa} \quad (56)$$

Deriving the fraction of k-time bonded molecules due to self and cross-association

Here, water is modeled as a hard sphere with four associating sites, where two of them (A and B) stand for the oxygen atom and the others (C and D) represent the hydrogen atoms. Alcohol is modeled with three associating sites, E and F representing the oxygen atom and G representing the hydrogen atom.

Using Wertheim's multi-density formalism, the contribution due to hydrogen bonding is composed of three main contributions: water-alcohol, water-water, and alcohol-alcohol which are written in equations (1), (2), and (3), respectively:

$$\frac{\Delta c^{(W-A)}}{V} = \left(\sigma_{\Gamma-A}^{(W)}\sigma_{\Gamma-G}^{(A)} + \sigma_{\Gamma-B}^{(W)}\sigma_{\Gamma-G}^{(A)} + \sigma_{\Gamma-C}^{(W)}\sigma_{\Gamma-E}^{(A)} + \sigma_{\Gamma-C}^{(W)}\sigma_{\Gamma-F}^{(A)} + \sigma_{\Gamma-D}^{(W)}\sigma_{\Gamma-E}^{(A)} + \sigma_{\Gamma-D}^{(W)}\sigma_{\Gamma-F}^{(A)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-A})} \tag{57}$$

$$\frac{\Delta c^{(W-W)}}{V} = \left(\sigma_{\Gamma-A}^{(W)}\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-B}^{(W)}\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-A}^{(W)}\sigma_{\Gamma-D}^{(W)} + \sigma_{\Gamma-B}^{(W)}\sigma_{\Gamma-D}^{(W)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-W})} \tag{58}$$

$$\frac{\Delta c^{(ET-A)}}{V} = \left(\sigma_{\Gamma-E}^{(A)}\sigma_{\Gamma-G}^{(A)} + \sigma_{\Gamma-F}^{(A)}\sigma_{\Gamma-G}^{(A)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{A-A})} \tag{59}$$

In the equations above, $\sigma_{\Gamma-A}^{(W)}$ is the density of water molecules not bonded at site A. Other density factors are defined in a similar way. $\Delta_{\mathbf{SAFT}}^{(\mathbf{W-A})}$ is the water-alcohol hydrogen bond strength.

In Wertheim's theory, the derivatives of the contributions with respect to the density factors need to be evaluated to calculate the fractions of molecules at different bonding states:

$$c_A^{(W)} = \left(\sigma_{\Gamma-G}^{(A)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-A})} + \left(\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-D}^{(W)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-W})} \tag{60}$$

$$c_B^{(W)} = \left(\sigma_{\Gamma-G}^{(ET)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-A})} + \left(\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-D}^{(W)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-W})} \tag{61}$$

$$c_C^{(W)} = \left(\sigma_{\Gamma-E}^{(A)} + \sigma_{\Gamma-F}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-A}^{(W)} + \sigma_{\Gamma-B}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{62}$$

$$c_D^{(W)} = \left(\sigma_{\Gamma-E}^{(A)} + \sigma_{\Gamma-F}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-A}^{(W)} + \sigma_{\Gamma-B}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{63}$$

$$c_E^{(A)} = \left(\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-D}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-G}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \tag{64}$$

$$c_F^{(A)} = \left(\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-D}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-G}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \tag{65}$$

$$c_G^{(A)} = \left(\sigma_{\Gamma-A}^{(W)} + \sigma_{\Gamma-B}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-E}^{(A)} + \sigma_{\Gamma-F}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \tag{66}$$

Defining $X_G^{(A)} = \sigma_{\Gamma-G}^{(A)} / \rho^{(A)}$ as an example to substitute the density factors with fractions:

$$c_A^{(W)} = \rho^{(A)}\left(X_C^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{67}$$

$$c_B^{(W)} = \rho^{(A)}\left(X_G^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{68}$$

$$c_C^{(W)} = \rho^{(A)}\left(X_E^{(A)} + X_F^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(W)}\left(X_A^{(W)} + X_B^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{69}$$

$$c_D^{(W)} = \rho^{(A)}\left(X_E^{(A)} + X_F^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(W)}\left(X_A^{(W)} + X_B^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{70}$$

$$c_E^{(A)} = \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(A)}\left(X_G^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \tag{71}$$

$$c_F^{(A)} = \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(a)}\left(X_G^{(a)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \tag{72}$$

$$c_G^{(A)} = \rho^{(W)}\left(X_A^{(W)} + X_B^{(W)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-A})} + \rho^{(A)}\left(X_E^{(A)} + X_F^{(A)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{A-A})} \tag{73}$$

Using what is derived so far, the fractions of k-time bonded species are derived as following:

$$X_1^{(W)} = X_o^{(W)}\left(c_A^{(W)} + c_B^{(W)} + c_C^{(W)} + c_D^{(W)}\right) \tag{74}$$

$$X_2^{(W)} = X_o^{(W)}\left(c_A^{(W)}c_B^{(W)} + c_A^{(W)}c_C^{(W)} + c_A^{(W)}c_D^{(W)} + c_B^{(W)}c_C^{(W)} + c_B^{(W)}c_D^{(W)} + c_D^{(W)}c_C^{(W)}\right) \tag{75}$$

$$X_3^{(W)} = X_o^{(W)}\left(c_A^{(W)}c_B^{(W)}c_C^{(W)} + c_A^{(W)}c_B^{(W)}c_D^{(W)} + c_D^{(W)}c_B^{(W)}c_C^{(W)}\right) \tag{76}$$

$$X_4^{(W)} = X_o^{(W)}\left(c_A^{(W)}c_B^{(W)}c_C^{(W)}c_D^{(W)}\right) \tag{77}$$

$$X_1^{(A)} = X_o^{(A)}\left(c_E^{(A)} + c_F^{(A)} + c_G^{(A)}\right) \tag{78}$$

$$X_2^{(A)} = X_o^{(A)}\left(c_E^{(A)}c_F^{(A)} + c_E^{(A)}c_G^{(A)} + c_G^{(A)}c_F^{(A)}\right) \tag{79}$$

$$X_3^{(A)} = X_o^{(A)}\left(c_E^{(A)}c_F^{(A)}c_G^{(A)}\right) \tag{80}$$

Deriving the fraction of k-time bonded molecules due to self-association only

$$\frac{\Delta c^{(W-A)}}{V} = \left(\sigma_{\Gamma-A}^{(W)}\sigma_{\Gamma-G}^{(A)} + \sigma_{\Gamma-B}^{(W)}\sigma_{\Gamma-G}^{(A)} + \sigma_{\Gamma-C}^{(W)}\sigma_{\Gamma-E}^{(A)} + \sigma_{\Gamma-C}^{(W)}\sigma_{\Gamma-F}^{(A)} + \sigma_{\Gamma-D}^{(W)}\sigma_{\Gamma-E}^{(A)} + \sigma_{\Gamma-D}^{(W)}\sigma_{\Gamma-F}^{(A)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-A})} \tag{81}$$

$$\frac{\Delta c^{(W-W)}}{V} = \left(\sigma_{\Gamma-A}^{(W)}\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-B}^{(W)}\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-A}^{(W)}\sigma_{\Gamma-D}^{(W)} + \sigma_{\Gamma-B}^{(W)}\sigma_{\Gamma-D}^{(W)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-W})} \tag{82}$$

$$\frac{\Delta c^{(A-A)}}{V} = \left(\sigma_{\Gamma-E}^{(A)}\sigma_{\Gamma-G}^{(A)} + \sigma_{\Gamma-F}^{(A)}\sigma_{\Gamma-G}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \tag{83}$$

$$c_A^{(W)} = \left(\sigma_{\Gamma-G}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-D}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{84}$$

$$c_B^{(W)} = \left(\sigma_{\Gamma-G}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-D}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{85}$$

$$c_C^{(W)} = \left(\sigma_{\Gamma-E}^{(A)} + \sigma_{\Gamma-F}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-A}^{(W)} + \sigma_{\Gamma-B}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{86}$$

$$c_D^{(W)} = \left(\sigma_{\Gamma-E}^{(A)} + \sigma_{\Gamma-F}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-A}^{(W)} + \sigma_{\Gamma-B}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{87}$$

$$c_E^{(A)} = \left(\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-D}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-ET})} + \left(\sigma_{\Gamma-G}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \tag{88}$$

$$c_F^{(A)} = \left(\sigma_{\Gamma-C}^{(W)} + \sigma_{\Gamma-D}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-G}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \tag{89}$$

$$c_G^{(A)} = \left(\sigma_{\Gamma-A}^{(W)} + \sigma_{\Gamma-B}^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \left(\sigma_{\Gamma-E}^{(A)} + \sigma_{\Gamma-F}^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \tag{90}$$

$$c_A^{(W)} = \rho^{(A)}\left(X_G^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{91}$$

$$c_B^{(W)} = \rho^{(A)}\left(X_G^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{92}$$

$$c_C^{(W)} = \rho^{(A)}\left(X_E^{(A)} + X_F^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(W)}\left(X_A^{(W)} + X_B^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \tag{93}$$

$$c_D^{(W)} = \rho^{(A)}\left(X_E^{(A)} + X_F^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(W)}\left(X_A^{(W)} + X_B^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \quad (94)$$

$$c_E^{(A)} = \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(A)}\left(X_G^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \quad (95)$$

$$c_F^{(A)} = \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(A)}\left(X_G^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \quad (96)$$

$$c_G^{(A)} = \rho^{(W)}\left(X_A^{(W)} + X_B^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} + \rho^{(A)}\left(X_E^{(A)} + X_F^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{A-A})} \quad (97)$$

To distinguish between various bonding states, the derivatives are written in a way that can be easily understood:

$$c_A^{(W-W)} = \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \quad (98)$$

$$c_A^{(W-A)} = \rho^{(A)}\left(X_G^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} \quad (99)$$

$$c_B^{(W-W)} = \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \quad (100)$$

$$c_B^{(W-A)} = \rho^{(A)}\left(X_G^{(ET)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} \quad (101)$$

$$c_C^{(W-W)} = \rho^{(W)}\left(X_A^{(W)} + X_B^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \quad (102)$$

$$c_C^{(W-A)} = \rho^{(A)}\left(X_E^{(A)} + X_F^{(A)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-A})} \quad (103)$$

$$c_D^{(W-W)} = \rho^{(W)}\left(X_A^{(W)} + X_B^{(W)}\right)\Delta_{\mathrm{SAFT}}^{(\mathrm{W-W})} \quad (104)$$

$$c_D^{(W-A)} = \rho^{(A)}\left(X_E^{(A)} + X_F^{(A)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-A})} \tag{105}$$

$$c_E^{(ET-W)} = \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-A})} \tag{106}$$

$$c_E^{(A-A)} = \rho^{(A)}\left(X_G^{(A)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{A-A})} \tag{107}$$

$$c_F^{(A-W)} = \rho^{(W)}\left(X_C^{(W)} + X_D^{(W)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-A})} \tag{108}$$

$$c_F^{(A-A)} = \rho^{(A)}\left(X_G^{(A)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{A-A})} \tag{109}$$

$$c_G^{(A-W)} = \rho^{(W)}\left(X_A^{(W)} + X_B^{(W)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{W-A})} \tag{110}$$

$$c_G^{(A-A)} = \rho^{(A)}\left(X_E^{(A)} + X_F^{(A)}\right)\Delta_{\mathbf{SAFT}}^{(\mathbf{A-A})} \tag{111}$$

Where the fraction of alcohol molecules not bonded at site E is defined as $X_E^{(A)} = \sigma_{\Gamma-E}^{(A)}/\rho^{(A)}$. Consequently, the fractions of alcohol molecules that are k-time bonded to other alcohol molecules are derived as:

$$X_1^{(A)} = X_o^{(A)}\left(c_E^{(A-A)} + c_F^{(A-A)} + c_G^{(A-A)} + c_E^{(A-A)} * \left(c_F^{(A-W)} + c_G^{(A-W)}\right) + c_F^{(A-A)} * \left(c_E^{(A-W)} + c_G^{(A-W)}\right) + c_G^{(A-A)} * \left(c_F^{(A-W)} + c_E^{(A-W)}\right) + c_E^{(A-A)} c_F^{(A-W)} c_G^{(A-W)} + c_F^{(A-A)} c_E^{(A-W)} c_G^{(A-W)} + c_G^{(A-A)} c_F^{(A-W)} c_E^{(A-W)}\right) \tag{112}$$

$$X_2^{(A)} = X_o^{(A)}\left(c_E^{(A-A)} c_F^{(A-A)} + c_E^{(A-A)} c_G^{(A-A)} + c_G^{(A-A)} c_F^{(A-A)} + c_E^{(A-A)} c_F^{(A-A)} c_G^{(A-W)} + c_E^{(A-A)} c_G^{(A-A)} c_F^{(A-W)} + c_G^{(A-A)} c_F^{(A-A)} c_E^{(A-W)}\right) \tag{113}$$

$$X_3^{(A)} = X_o^{(A)}\left(c_E^{(A-A)} c_F^{(A-A)} c_G^{(A-A)}\right) \tag{114}$$