HOMOGENOUS NUCLEATION RATES OF ICE IN SUPERCOOLED BINARY LIQUID MIXTURES OF WATER + NON-ELECTROLYTES: A COMBINED THEORETICAL AND EXPERIMENTAL STUDY

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**List of Symbols**

- \( A \): Helmholtz free energy.
- \( A_n \): Surface area of an ice-embryo with size \( n \).
- \( b_0 \): Mole fraction of the non-bonded water molecules in 1 mole of hypothetical defect phase of liquid water.
- \( b_1 \): Mole fraction of the 1 H-bonded water molecules in 1 mole of hypothetical defect phase of liquid water.
- \( b_2 \): Mole fraction of the 2 H-bonded water molecules in 1 mole of hypothetical defect phase of liquid water.
- \( b_3 \): Mole fraction of the 3 H-bonded water molecules in 1 mole of hypothetical defect phase of liquid water.
- \( b_4 \): Mole fraction of the 4 H-bonded water molecules in 1 mole of hypothetical defect phase of liquid water.
- \( c_n \): Concentration of the critical ice nucleus in a given volume.
- \( c_{cr} \): Effective concentration of the critical ice nucleus, which are able to grow further in a given volume.
- \( \Delta g^* \): Free energy of activation for the diffusion of water molecules (across the ice-water interface).
- \( \Delta G_n \): Free energy of the formation of an ice-embryo with size \( n \).
- \( \Delta G_{cr} \): Free energy of the formation of a critical ice-nucleus.
- \( d_r \): The thickness of the surface layer on the outer shell of an ice-embryo.
- \( D \): Self diffusion constant of liquid water.
- \( E_A \): Activation energy of defect formation.
- \( E_0 \): Apparent H-bond energy per mole of liquid water.
- \( E_i \): H-bond energy in 1 mol of i-bonded water molecules.
- \( f \): The net flux of water molecules to the surface of a critical ice nucleus.
- \( f_v \): Molecular vibrational partition function for water molecules.
- \( f_r \): Molecular translational partition function for water molecules.
- \( f_p \): Molecular rotational partition function for water molecules.
- \( f_i \): Molecular partition function for i-bonded water molecules.
- \( g \): Also called as Eadie’s patch size. The total number of molecules included in a purely ice-like patch ignoring the molecules of hypothetical defect phase. It counts for the 4-bonded molecules in the bulk of an ice-like patch and the 2- and 3-bonded molecules on the surface of a patch.
- \( G \): Gibbs free energy.
- \( g_2 \): The number 2 H-bonded molecules on the surface of an ice-like patch before the interaction of surface molecules with the adhering non-bonded molecules of the interphase.
- \( g_3 \): The number 3 H-bonded molecules on the surface of an ice-like patch before the interaction of surface molecules with the adhering non-bonded molecules of the interphase.
- \( g_4 \): The number of 4 H-bonded molecules in an ice-like patch.
- \( g_{2 \rightarrow 3} \): Number of 2-bonded molecules becoming 3-bonded with the attachment of a non-bonded molecule from the interphase in between the patches.
- \( g_{2 \rightarrow 4} \): Number of 2-bonded molecules becoming 4-bonded with the attachment of a non-bonded molecule from the interphase in between the patches.
- \( g_{3 \rightarrow 4} \): Number of 3-bonded molecules becoming 4-bonded with the attachment of a non-bonded molecule from the interphase in between the patches.
- \( g(y) \): Combinatorial factor in the partition function, which counts for all possible configurations for a given state of having composed of ceratin mole fractions of different H-bonded water molecules.
- \( G_2 \): The number 2 H-bonded molecules on the surface of an ice-like patch after the interaction of surface molecules with the adhering non-bonded molecules of the interphase.
- \( G_3 \): The number 3 H-bonded molecules on the surface of an ice-like patch after the interaction of surface molecules with the adhering non-bonded molecules of the interphase.
- \( G_4 \): The number 4 H-bonded molecules on the surface of an ice-like patch after the interaction of surface molecules with the adhering non-bonded molecules of the interphase.
- \( h_0 \): Fractions of non-bonded water molecules in a 1 mole of liquid water.
- \( h_1 \): Fractions of 1-bonded water molecules in a 1 mole of liquid water.
- \( h_2 \): Fractions of 2-bonded water molecules in a 1 mole of liquid water.
- \( h_3 \): Fractions of 3-bonded water molecules in a 1 mole of liquid water.
- \( h_4 \): Fractions of 4-bonded water molecules in a 1 mole of liquid water.
- \( I_z \): Moment of inertia about the z axis.
- \( j \): Actual number of H-bonds a water molecule forms with its neighbors, which depends on its coordination environments. It varies between 0 and 4.
### List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J$</td>
<td>Temperature dependent nucleation rate expressed as number of germs formed per unit volume per unit time.</td>
</tr>
<tr>
<td>$J_L$</td>
<td>Nucleation rate calculated from the slope of a linear segment which occurs left to a knick (short-time region) in an ln $N_e/N_0$ vs $V_d$ t diagram.</td>
</tr>
<tr>
<td>$J_R$</td>
<td>Nucleation rate calculated from the slope of a linear segment which occurs right to a knick (long-time region) in an ln $N_e/N_0$ vs $V_d$ t diagram.</td>
</tr>
<tr>
<td>$k$</td>
<td>Rate constant.</td>
</tr>
<tr>
<td>$n_i$</td>
<td>The number of water molecules in a patch (or on the surface of agglomerates) which belong to the hypothetical phase of defects.</td>
</tr>
<tr>
<td>$n_d$</td>
<td>Mole fraction of hypothetical defect phase in liquid water.</td>
</tr>
<tr>
<td>$n_4$</td>
<td>Number of 4-bonded molecules in an ice-embryo.</td>
</tr>
<tr>
<td>$n_{interface}$</td>
<td>Number of water molecules found in the interphase adherent on the surface of a patch.</td>
</tr>
<tr>
<td>$n_e$</td>
<td>Number of water molecules on a unit area on a patch surface.</td>
</tr>
<tr>
<td>$n_{total}$</td>
<td>Total number of molecules including the four-bonded molecules in the inner-shell, and defect molecules on the surface, in an ice-embryo.</td>
</tr>
<tr>
<td>$N$</td>
<td>Total number of water molecules in a system.</td>
</tr>
<tr>
<td>$N_A$</td>
<td>Avagadro’s number.</td>
</tr>
<tr>
<td>$N_{Agg-S}$</td>
<td>Number of 4-bonded agglomerates (or ice embryos) placed at the surface of a patch.</td>
</tr>
<tr>
<td>$N_{Agg-T}$</td>
<td>Total number of four-bonded agglomerates present in a patch.</td>
</tr>
<tr>
<td>$N_c$</td>
<td>Number of water molecules in contact with the unit surface area of an ice embryo.</td>
</tr>
<tr>
<td>$N_i$</td>
<td>The number of i-bonded water molecules in 1 mole of liquid water.</td>
</tr>
<tr>
<td>$m$</td>
<td>Molecular mass of a water molecule.</td>
</tr>
<tr>
<td>$\mu_{liq}$</td>
<td>Chemical potential, i.e. Molar Gibbs free energy of liquid water.</td>
</tr>
<tr>
<td>$\mu_{ice}$</td>
<td>Chemical potential, i.e. Molar Gibbs free energy of ice.</td>
</tr>
<tr>
<td>$\mu_d$</td>
<td>Chemical potential, i.e. Molar Gibbs free energy of the hypothetical defect phase.</td>
</tr>
<tr>
<td>$\Delta\mu_{ice-liq}$ (or $\Delta\mu$)</td>
<td>$\mu_{ice} - \mu_{liq}$</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Symmetry number.</td>
</tr>
<tr>
<td>$\sigma_{lw}$</td>
<td>Surface tension of the ice-water interface on a growing ice embryo.</td>
</tr>
<tr>
<td>$P_{diff}$</td>
<td>The probability that a molecule will diffuse out is lattice point.</td>
</tr>
<tr>
<td>$p$</td>
<td>H-bond formation probability in the hypothetical phase of lattice defects in liquid water.</td>
</tr>
<tr>
<td>$P_{rel(n)}$</td>
<td>Probability of finding an ice embryo of size n in a patch</td>
</tr>
<tr>
<td>$\rho_l$(liq)</td>
<td>Density of liquid water at a given temperature T.</td>
</tr>
<tr>
<td>$\rho_l$(ice)</td>
<td>Density of ice at a given temperature T.</td>
</tr>
<tr>
<td>$\rho_d$(d)</td>
<td>Density of hypothetical defect phase at a given temperature T.</td>
</tr>
<tr>
<td>$r_{inner-shell}$</td>
<td>Radius of the inner shell of a patch below its adherent interphase.</td>
</tr>
<tr>
<td>$r_{patch}$</td>
<td>Radius of a patch having a spherical geometry.</td>
</tr>
<tr>
<td>$R_{agg}$</td>
<td>The radius of the inner-shell of an ice-embryo.</td>
</tr>
<tr>
<td>$r(T)$</td>
<td>Van der Waals radius of the water molecule in ice at a given temperature.</td>
</tr>
<tr>
<td>$s$</td>
<td>Total number of assigned vibrational frequencies for a water molecule, which depends on its H-bonding state.</td>
</tr>
<tr>
<td>$S$</td>
<td>Entropy.</td>
</tr>
<tr>
<td>$S_{total}$</td>
<td>Total patch size, i.e. Total number of 4-bonded molecules and the molecules with less than 4-Hydrogen bonds which constitutes a patch and its adherent interface.</td>
</tr>
<tr>
<td>$t_s$</td>
<td>Lifetime of the metastable state in liquid water.</td>
</tr>
<tr>
<td>$t_{rel}$</td>
<td>The relaxation time of the metastable state in liquid water.</td>
</tr>
<tr>
<td>$&lt;t&gt;$</td>
<td>Average mean passage time for the water molecules to leave a surface layer of certain thickness.</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$U$</td>
<td>Internal energy.</td>
</tr>
<tr>
<td>$\chi_H$</td>
<td>The electronegativity of the hydrogen atom.</td>
</tr>
<tr>
<td>$X_i$</td>
<td>Mole fraction of ice-like phase in liquid water.</td>
</tr>
<tr>
<td>$\chi_O$</td>
<td>The electronegativity of the oxygen atom.</td>
</tr>
<tr>
<td>$V_d$</td>
<td>Packing volume of a water molecule that belong to the hypothetical defect phase.</td>
</tr>
<tr>
<td>$V_c$</td>
<td>Free volume of a water molecule in a translational motion.</td>
</tr>
</tbody>
</table>
List of Symbols

\[ V_m(d): \] Molar volume of the hypothetical defect phase.
\[ V_{\text{ice}}: \] Packing volume of a water in ice.
\[ V_m(\text{ice}): \] Molar volume of ice.
\[ V_{\text{patch}}: \] Total volume of a patch assuming a spherical geometry.
\[ V_{\text{surf}}: \] The volume of the surface layer of with a thickness \( dr \) for a spherical agglomerate.
\[ W_{\text{eff}}: \] Total effective surface area available for the growth of four-bonded agglomerates (ice-embryos) on the surface of a patch.
\[ \Omega_{\text{eff}}: \] The effective surface area for the growth of an agglomerate, which lies near to the surface.
\[ \Omega_{\text{t}}: \] The surface area of the critical ice nucleus.
\[ W_{\text{patch}}: \] Surface area of the inner shell of a patch just below its adherent interface.
\[ z: \] Maximum number of H-bond that water can form with its nearest neighbors in liquid water (\( z=4 \)).
\[ Z: \] Canonical partition function of liquid water.
\[ Z: \] The Zeldovitch factor
\[ Z(\text{avg}): \] Canonical partition function of an ice embryo, with the most probable size.
\[ Z(n): \] Canonical partition function of an ice embryo, which consists of \( n \) water molecules.