Chapter 6: Summary / Zusammenfassung

Summary

1. In this study, the models describing the structure of liquid water have been presented critically. It is seen that it is not possible to calculate homogeneous nucleation rates of ice in supercooled liquid water by using any one of the available models. A modified model of liquid water structure has been developed to calculate the homogenous nucleation rates. The principal features of this model are the following:

   - Liquid water has a microheterogeneous structure, which consists of big patches containing several thousands of water molecules.
   - These patches contain agglomerates of water with ice-like structure.
   - We assume that between the patches there is no direct interaction. However the space in between the patches is filled by an interphase, which contains non-bonded and mobile water molecules.
   - The quantification of structural parameters is based on statistical thermodynamics. In carrying out the calculations, we introduced a hypothetical phase of lattice defects, which circumvents the qualification of lattice defects. It allows a proper description of LDL-, HDL- patches, and the interphase.

2. The critical ice nucleus is defined by thermodynamics; its evaluation however is a kinetic problem. Critical ice germs grow from the ice-like agglomerates. The growth rate depends on the position of agglomerates in the patches. It is governed by the addition of water molecules from the interphase.

3. The successful fit of the calculated nucleation rates to the experimentally obtained values is possible with reasonable values of the following parameters: The thickness of the surface layer of agglomerates and the fraction of ice-like molecules in the patches.

4. In aqueous binary mixtures with different non-electrolytes, the nucleation rate at a given state of supercooling is lower in comparison to water. The lowering of the nucleation rates at low

solute concentration (x_2 = 0.002), i.e. 1 solute molecule per 500 molecules of water can only be explained by assuming a considerable enrichment of solute molecules in the interphase between the patches. This supports the proposal that the formation of the critical ice germs occurs preferably at the surface of patches.

5. The nucleation in aqueous mixtures containing higher concentration of dioxane reveals a change of the nucleation mechanism near x_2 = 0.30. The nucleation rates first decreases with increasing concentration and increase after this composition.

6. The experimental values of the nucleation rates of pure water and water/dioxane mixtures have been controlled by measuring in two different electrodynamic traps. There is little difference in the results, probably due to the control and measurement of the temperature.

Finally, the impact of the proposed model of liquid water on the discussion of confined water and of water in biological systems is still open.

Zusammenfassung

1. Die Modelle zur Struktur von flüssigem Wasser werden kritisch dargestellt. Es zeigt sich, daß mit keinem der verfügbaren Modelle homogene Nukleationsraten von Eis in unterkühltem Wasser berechnet werden können. Es wurde ein modifiziertes Modell der Struktur von flüssigem Wasser entwickelt, das die Berechnung von homogenen Nukleationsraten erlaubt. Die wichtigsten Merkmale dieses Modells sind folgende:

   - Flüssiges Wasser besitzt eine mikroheterogene Struktur, die aus großen „Patches“ von mehreren tausend Wassermolekülen besteht.
   - Diese „Patches“enthalten so genannte Agglomerate, die Eisstruktur besitzen.
   - Wir nehmen an, daß zwischen den „Patches“ keine direkte Wechselwirkung besteht. Der Raum zwischen den „Patches“ wird durch eine Zwischenphase erfüllt, die nichtgebundene und mobile Wassermoleküle enthält.
   - Die Quantifizierung der Strukturparameter basiert auf Statistischer Thermodynamik. Zur Durchfühlung von Berechnungen, haben wir eine hypothetische Phase von Gitterdefekten eingeführt, mit der man ihre detailierte Spezifikation vermeidet. Sie erlaubt jedoch eine angemessen Beschreibung von LDL- und HDL-„Patches“.

2. Der kritische Eiskeim ist thermodynamisch definiert. Seine Entwicklung jedoch ist ein kinetisches Problem. Kritische Eiskeime entstehen durch Wachstum der eisähnlichen Agglomerate. Die Wachstumsrate hängt von der Position der Agglomerate in den „Patches“ ab. Sie wird kontrolliert durch die Anlagerung von Wassermolekülen aus der Zwischenphase.

3. Die erfolgreiche Anpassung der berechneten Nukleationsraten an die experimentellen Werte ist möglich mit plausiblen Werten der folgenden Parameters: Dicke der Oberflächenschicht der Agglomerate und dem Anteil der eisartig gebundenen Wassermoleküle in den „Patches“.

4. In wässrigen binären Mischungen mit verschiedenen ‚Nichtelektrolyten’ ist die Nukleationsrate bei definierter Unterkühlung erniedrigt im Vergleichzu reinem Wasser. Die

Absenkung der Nukleationsraten bei niedriger Konzentration (x_2 = 0.002) der Nichtelektrolyt-Komponente (1 Molekül Nichtelektrolyt per 500 Wassermoleküle) kann nur damit erklärt werden, daß diese in der Zwichenphase zwischen den „Patches" erheblich angereichert werden; dies unterstützt die Ansicht , daß die Bildung kritischer Eiskeime vorzugsweise an der Oberfläche der „Patches" stattfindet.

5. Die Nukleation in wässrigem Dioxan zeigt bei hoher Dioxankonzentration (x_2 ~ 0.30) einen Wechsel ihres Mechanismus. Die Nukleationsraten nehmen zunächst ab und nehmen ab x_2 ~ 0.30 wieder zu.

6. Die experimentellen Werte der Nukleationsraten in reinem Wasser und Wasser/Dioxan werden durch Messung in zwei verschiedenen elektrodynamischen Fallen kontrolliert. Die Resultate unterschieden sich nur wenig , was möglicherweise auf die Temperaturkalibrierung und -messung zurückzuführen ist.

Abschileßend sei angemerkt, dass die Bedeutung des vorgeschlagenen Wassermodells für die Diskussion von „confined water" und von Wasser in biologischen Systemen noch offen ist.

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