

Freezing-point depression by insoluble impurities: A finite size effect

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Salt in water is used as anti-freeze protection. The freezing point of the water/salt system is lowered by the effort to transform the homogeneous solution into separated phases of purified ice and concentrated brine. Insoluble impurities, by contrast, cannot influence the freezing point of a macroscopic liquid, which forms instead two separated and independent phases. However, in a nano-sized particle the phases lose their independence, since their interfacial energy can no longer be neglected. Furthermore this surface contribution can change upon melting. Typically, it decreases as a possible lattice mismatch of the solid can be compensated by the higher structural freedom of the liquid, which thus becomes more favorable. It occupies a larger temperature range in the phase-diagram and the freezing points are depressed.

We illustrate this cluster-specific effect by studying nano particles of the sodium – sodium oxide binary system both experimentally and theoretically. First-principles density functional theory is employed. Bulk sodium hardly solves its oxide, which thus cannot depress the freezing point. In contrast our thermodynamic experiments show that the oxide in sodium clusters systematically depresses both freezing points and latent heats and that this effect increases with the size of the oxide. Our calculations confirm that this is due to the surface tension between the oxide and metal in the solid clusters. The surface energy is released under melting and promotes the liquid phase thermodynamically. This causes the observed, cluster-specific freezing point depression.

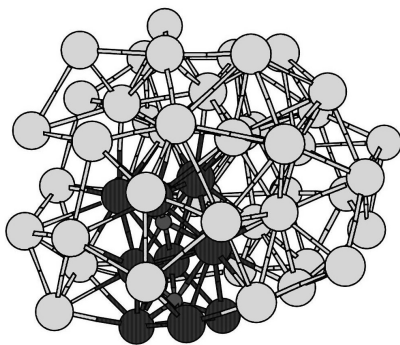


Figure: Na_{55}O_2 at 340 K: The pure liquid metal (light gray circles) forms a well-separated phase that only partially wets the oxide (small dark circles: oxygen; big dark circles: sodium.). Even though the metal cannot dissolve the oxide, its freezing point is depressed by the surface tension between the phases that increases under freezing.