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Melting and Glass Transition as Mixing Processes

by
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Abstract
Melting of chemically bonded solids has been explained recently by transitions of electrons in higher electron states. Such transitions are shown to cause decomposition of the crystals into many units or sub-systems build-up of one or few atoms that mix in the melt. Most chemical elements possess molar melting entropies, ΔS_m, in the order of the universal molar gas constant, R, or less, which is expected for mixing of a small number of differing groups of particles totalling one mole. Only in the case of crystals with bonding via sp^3- and similar hybrids the molar melting entropy is much larger. This observation can be interpreted by a massive change of the phonon spectra of the melting solids in addition to the decomposition into mixing units. Upon cooling the melt below the glass transition temperature, T_g, the mixed decomposition products of the melt are frozen in. This frozen-in mixing entropy cannot be removed from the undercooled melt and - finally - the glass by thermal conduction and remains stored in the glass until the absolute zero of the temperature. Removal of the mixing entropy is possible only by reordering of the constituents or crystallisation.

Since the entropy is frozen-in near and above T_g not only entropy but also enthalpy is frozen-in, which is often neglected in the literature. The specific amounts of the entropy and enthalpy frozen-in are not unique for a given glass but depend on the status of relaxation.