Thermodynamic aspects of melting and glass formation

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Abstract

Glasses are mostly produced by cooling from the melt. In order to understand the mechanism of melting and glass formation, the enthalpy function and the specific heat capacities of one-component systems have been analysed. In many cases, the specific heat capacity due to atomic vibrations is increased near the melting transition by a contribution due to electronic transitions from low to high energy levels. These electronic transitions, which increase with the temperature, are accompanied by a change of the corresponding wave-functions and of the local charge distributions. The charge distribution changes according to the random time series of the different occupied electronic states and drives the core ions to new positions. If the forces are strong enough and the core ions relax to their new positions within the lifetime of the excited states, we have a changing arrangement of the core ions or a melt.

The distribution of the electronic energy levels in the molten state differs from that of the crystalline solid, since the arrangement of the core ions is non-periodic. With decreasing temperature the electrons relax to lower states of the disordered arrangement. If the forces of the corresponding charge distribution are too weak to attract the core ions to new and regular positions, the transformation into a glass takes place. Thus, electronic transitions to higher energy states freeze out near the glass transformation temperature and the disorder of the constituting core ions becomes fixed. This is supported by sufficiently strong directional bonds between neighbouring constituents and a low melting entropy.