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# Chapter 12: Thermodynamics of Melting and the Formation of Glasses and Crystals

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**Abstract:** To understand the mechanism of melting, the enthalpy functions and the specific heat capacities of about 450 one-component systems have been analyzed. In many cases, the specific heat capacity of the bonding electrons cannot be neglected near the melting transition. Thus, electrons make transitions from low to high energy levels with increasing temperature. The transitions into higher states cause a change of the wave-functions and of the spatial probability distributions. The charge probability distribution changes according to the random time series of electronic transitions into different 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 with respect to both energy and space. With decreasing temperature the electrons relax to lower states of the disordered arrangement. If the forces are too weak to attract the core ions to new and regular positions, the transition into a glass takes place. Thus, electronic transitions to higher energy states with a large change of the charge probability density freeze out near the glass transformation temperature and the disorder of the constituting ions becomes fixed. This is supported by sufficiently strong directional bonds between neighbouring atoms and a low melting entropy per atom. On the other hand, the symmetry of the wave-functions may induce ordering of the nearest neighbours in the melt and crystallisation in the range of undercooling. This is supported if the melting entropy per atom is large.

Several further effects observed near the glass transformation, such as relaxation processes and the change of the thermal expansion, can be understood without difficulties by the interaction of the outer electrons in low and excited energy states in the potential of the ensemble of the vibrating core ions.

**Keywords:** melting, glass transition, enthalpy, entropy, phase transition, order-disorder effects