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The non-extensive spinodal line: implications for the early stage solid-solid precipitation in alloys

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Abstract – Non-equilibrium thermodynamic processes are characterized by deviations from Boltzmann´s distribution for the microstates, which leads to the breakup of extensivity of thermodynamic state variables. Tsalllis´method allows to take account of this effect by introducing a parametric expression for the system´s entropy. The authors had shown previously that Tsallis´ entropy allows to move the spinodal line arbitrarily close to the binodal lines of a phase separating phase diagram in the Bragg-Williams approximation and interpreted experimental findings on the early stage precipitation in metallic alloys. The present work investigates this effect using the Bethe approximation.

Non-extensive thermodynamics is a recently developed theoretical field of statistical physics. It aims at describing the thermodynamics of systems in which the extensivity hypothesis fails[1]. One of the ways to produce non-extensivity is to depart from the Boltzmann´s distribution of microstates (i.e. Going non-equilibrium) and this is a characteristic of the precipitation process in alloys, where a high temperature equilibrium state (Boltzmann distributed at high temperature) is quenched to a lower temperature, turning into a non-equilibrium state, which slowly evolves towards the low temperature Boltzmann distribution. Tsallis´ formalism is a simple method to generate a non-extensive thermodynamics using a parametric (q) redefinition of the entropy (Boltzmann´s formalism is a special case of Tsallis´ in the limit $q \rightarrow 1$). Curado and Tsallis worked out the connection between thermodynamics and this non-extensive entropy[1], and provided the basis in which standard statistical mechanical problems can be solved.

One of the present authors, investigating the early stage of precipitation in metallic alloys close to the binodal lines of the phase diagrams, observed deviations form the behavior expected using standard Nucleation and Growth (NG) theories, in the sense that nucleation took considerably less time to occur than predicted [2]. This author showed that these deviations could be rationalized if the precipitation could be considered to proceed via the continuous amplification of concentration waves in the homogeneous non-equilibrium solid solution (i.e. via spinodal decomposition) and not by thermally activated nucleation[2]. The question on how spinodal decomposition could take place well inside the metastability domain was justified by a simple Bragg-Williams calculation using Tsallis entropy, where it was shown that the position of the spinodal line (that is, the boundary between the metastable and unstable regions in the phase diagram) could be move arbitrarily closer to the binodal line by a proper choice of q[3]. The Bragg-Williams formalism, however, is rather crude and therefore the present authors derived Tsallis´ formalism in the pair approximation (Bethe approximation) using two theoretical methods [4]. This, however, introduced a considerable complexity in the model and the equations become dependent on the system´s size (defined as the number of atoms, N).

The present work revisits to the original problem of determining the q dependency of the position of the spinodal line, but now in the pair approximation. The basic equations are derived and an algorithm based on the Cluster Variation Method is proposed. Using this algorithm the spinodal line can be numerically calculated and the q dependency investigated. The question of the size dependency of the solution is discussed, since one of the theoretical procedures used in ref. [4] showed that this dependency must vanish, even if this not as clear as it appears using the CVM formalism.

References

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