

PHASE DIAGRAMS AND GRAIN SIZE: A FEW REMARKS

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The relations among phases P_i in a phase diagram basically reflect the properties of the Gibbs energy functions: $g_i = u_i + Pv_i - Ts_i$, with u_i internal energy, v_i molar volume and s_i molar entropy of phase P_i ; P is pressure and T temperature. If we consider that solid phase P_i is present in the system as a set of spherical particles with same radius R and if we take into account the surface energy, we can modify g_i as $g_i = u_i + Pv_i - Ts_i + A.S_i. 1/R$ where S_i is the energy per unit surface of P_i and A a constant. One can thus formally consider $1/R$ on the same footing as other thermodynamic parameters such as P or T and *draw phase diagrams with $1/R$ as a parameter*. This may be done provided all the phases of a given system have approximately the same radius at equilibrium. This can be observed from many natural or industrial systems where the grain size is approximately uniform: this implies that the different phases have the same “history”, i.e. they have grown together. Several applications of this approach will be given : - drawing phase diagrams for systems with low cristallinity or involving small grains (nanosystems, cements) and compare with the same system with coarser grains; - studying the early stages of crystal growth (role of nucleation, precursors, early disordered or poorly ordered phases, oversaturation and grain size; application to SiO_2 polymorphs); - discussing some kinetic aspects; - discussing the role of the interface curvature (with R possibly negative) and the explanation of some textures in natural systems. D. Garcia is thanked for helpful comments.