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A Heuristic Theory of Phase Transitions

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Abstract. Let Z be a suitable Banach space of interactions for a lattice spin system. If $n+1$ thermodynamic phases coexist for $\Phi_0 \in Z$, it is shown that a manifold of codimension n of coexistence of (at least) $n+1$ phases passes through Φ_0. There are also $n+1$ manifolds of codimension $n-1$ of coexistence of (at least) n phases; these have a common boundary along the manifold of coexistence of $n+1$ phases. And so on for coexistence of fewer phases. This theorem is proved under a technical condition (R) which says that the pressure is a differentiable function of the interaction at Φ_0 when restricted to some codimension n affine subspace of Z. The condition (R) has not been checked in any specific instance, and it is possible that our theorem is useless or vacuous. We believe however that the method of proof is physically correct and constitutes at least a heuristic proof of the Gibbs phase rule.

0. Introduction

The aim of this article is to try to explain the Gibbs phase rule in statistical mechanics. We shall for definiteness consider the statistical mechanics of a lattice spin system. Let $n+1$ phases (labelled $0, 1, \ldots, n$) coexist for an interaction Φ_0. If Φ_0 lies in a suitable space Z of interactions, the Gibbs phase rule can be expressed as follows.

a) There passes through Φ_0 a manifold V, of codimension n, of coexistence of at least $n+1$ phases.

b) For every non-empty subset $K=\{i_0, i_1, \ldots, i_k\}$ of $\{0, 1, \ldots, n\}$ there is near Φ_0 a manifold-with-boundary V_K of coexistence of at least $k+1$ phases; V_K has codimension k and its boundary is the union of the V_J with $J \supset K$, $J \neq K$.

c) There is a homeomorphism h of a neighborhood $\mathcal{O}$ of Φ_0 to a neighborhood of Φ_0 such that h is tangent to the identity at Φ_0, and $h^{-1} V_K$ is (locally) a convex polyhedral cone.

We shall prove that the Gibbs phase rule holds in the above sense if a certain condition (R) of *regular behavior* of the pressure near Φ_0 is satisfied. Unfortunately, as this is written, (R) has not been verified in any example, and it is thus conceivable