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On Thermodynamic Stability Theory

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Abstract

The necessary and sufficient conditions for stability of non-equilibrium systems are derived using a novel and simple approach. The resulting inequalities, based on the postulate of local equilibrium, include the equilibrium stability criteria proposed previously by Gibbs, and Landau and Lifshitz as special cases as well as the Glansdorff-Prigogine stability criterion for non-equilibrium systems. Difficulties associated with the introduction of mathematical definitions for stability of motion in the context of thermodynamics are exemplified and a kinetic potential is proposed.

Introduction

The original stability criterion for equilibrium states proposed by Gibbs [1] states that a homogeneous system is stable if for arbitrary perturbations

$$\Delta E + P\Delta V - T\Delta S - \sum_{i=1}^{n} \mu_i \Delta m_i > 0\,, \tag{1}$$

where E, V, S, and m_i denote, respectively, total energy, volume, entropy, and mass of component i; T, P, and μ_i are temperature, pressure and chemical potential of component i. Landau and Lifshitz [2] employed the Maxwell and Gouy Theorem [3]

$$\Delta(E + P_0 V - T_0 S) > 0 \tag{2}$$

to derive stability conditions for systems with identical particles. They also showed that a stable binary mixture with a fixed number of moles of solvent satisfies the inequality

$$\Delta(E + P_0 V - T_0 S - \mu_0' N) > 0 \tag{3}$$

where T_0, and P_0 are temperature, and pressure of an external medium and μ_0' is the chemical potential of the solute in the medium.