RELATIONS BETWEEN THE RELAXATION THEORY IN DENSE FLUIDS AND THE NOTION OF NATURAL BREADTH OF SPECTRAL LINES

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The natural breadth ∇_μ of a spectral line is determined by the irreversible nature of the interaction between a frequency (ν_i) of the electro-magnetic field and all the other frequencies which occurs by the intermediary of one of the energy levels of an atom. The classical result is obtained when all the frequencies (ν_i and ν_R) are originally void of photons. According to this result ∇_ν is the transition probability by spontaneous emission of atoms per unit time (1).

Since the relaxation of a physical system S_1 in interaction with a heat bath S_2 is essentially determined by the irreversible character of the interaction between S_1 and S_2, one may hypothesize a close analogy between the relaxation time τ_i and the quantity ∇_ν^{-1} as defined above. This analogy is studied by elaborating a classical theory of relaxation of S_1, by developing the density function in phase space in a series of functions in terms of Liouville operators relating to S_1 and S_2. Contrary to the theory of irreversible phenomena as developed by Prigogine (2), the angular variables and the moment variables are not introduced. This permits the derivation of a simple expression for the relaxation time τ_i and the examination of analogies between the relaxation phenomenon and the natural width of spectral lines.

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(1) HEITLER : The quantum theory of radiation, Clarendon Press 1954, p. 182

(2) PRIGOGINE : Non equilibrium statistical mechanics; Interscience Publisher, 1962, chapitre 2.