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Statistical Mechanics of Quantum Mechanical Particles with Hard Cores

I. The Thermodynamic Pressure

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Abstract. The definition of the thermodynamic pressure of a quantum mechanical system of hard core particles is considered for a wide variety of boundary conditions and a large class of interactions. It is shown that the pressure can be defined for elastic walls and that in the limit of an infinite system the thermodynamic pressure both exists and is independent of the coefficient of elasticity. Similarly if repulsive wall boundary conditions are used the thermodynamic pressure exists. Unfortunately it has not been possible to demonstrate that the two pressures obtained are identical but a number of their properties and interrelationships are established.

1. Introduction

In this, and a subsequent, paper we extend to quantum hard core systems various results which have been obtained for classical [1–3] and quantum [4–6] spin systems and classical hard core systems [7]. In this paper we consider properties of the thermodynamic pressure.

To define the thermodynamic pressure one must first consider a finite system and this leads to a certain ambiguity concerning the choice of boundary conditions, which, in the quantum mechanical formalism, is related to the choice of the Hamiltonian. We consider Hamiltonians with a large class of stable interactions whose domains are specified by conditions of the form

$$\frac{\partial \Psi}{\partial n} = \sigma \Psi$$

on the boundary of the system; $\partial \Psi/\partial n$ denotes the normal derivative across the boundary of a wave function Ψ. The parameter σ introduced in this manner is related to the elasticity of the walls of the system, $\sigma = 0$ is perfect elasticity, $\sigma = \infty$ infinite repulsion, and $\sigma = -\infty$ infinite attraction. We prove that for finite σ the thermodynamic pressure exists and is independent of σ. This generalizes the result obtain by Ruelle [8]