Commun. math. Phys. 26, 53—77 (1972)

Thermodynamic Limit for Classical Systems with Coulomb Interactions in a Constant External Field

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Received November 16, 1971, in revised form January 11, 1972

Abstract. We introduce a new method for studying the thermodynamic limit for systems of particles with Coulomb interactions. The method is based on calculating the potential energy of the Coulomb interactions from the electric or magnetic fields in the system rather than from the energy of the individual particle – particle interactions. We are able to include the effects of a constant external field being imposed at the boundary of the system. The difficulties associated with Coulomb potentials being not even weakly tempered are overcome by imposing the boundary condition that at the boundary of the region containing the particles, the electric or magnetic field has normal component equal to that of the applied field. We prove that the thermodynamic free energy density exists and is independent of the sequence of regions used to define the limit. We introduce sequences of regions all of the same shape and show that for these sequences of regions the thermodynamic free energy density is independent of shape. Finally, we prove that the thermodynamic free energy is a convex function of the density of particles and of the applied field.

I. Introduction

In this paper we describe a new method for proving the existence of thermodynamic functions for systems where the interactions between the particles or molecules of the system include long range Coulomb forces and where in addition external electric or magnetic fields may be present. The interactions we consider include the forces between magnetic dipoles in paramagnets and ferromagnets, the forces between electric dipoles in dielectrics and the forces between charged particles in ionic systems. However, we specifically exclude from consideration interactions attributable to the interference of electric and magnetic fields, such as the interactions of charged particles with magnetic fields produced by electric currents; in consequence our treatment does not apply to diamagnetic substances. In addition to proving the existence of the free energy for such systems, we discuss rigorously some of the simple properties of the free energy. The method also makes it possible to include in