The Independence on Boundary Conditions for the Thermodynamic Limit of Charged Systems *

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Abstract: We study systems containing electrons and nuclei. Based on the fact that the Thermodynamic limit exists for systems with Dirichlet boundary conditions, we prove that the same limit is obtained if one imposes other boundary conditions such as Neumann, periodic, or elastic boundary conditions. The result is proven for all limiting sequences of domains which are obtained by scaling a bounded open set, with smooth boundary, except for isolated edges and corners.

1. Introduction

We consider systems composed of electrons and nuclei, i.e., point particles which interact via Coulomb interaction with the negatively charged particles being fermions. Due to their important role in describing nature, such systems have been intensively investigated. In particular, the thermodynamic limit, i.e., the limit in which the system becomes large, has been studied extensively in [1]. In that work, it was shown that the thermodynamic limit exists for thermodynamic quantities, such as the pressure and the free energy density, provided that they are defined using Dirichlet boundary conditions. Furthermore, it was shown that these quantities possess the properties which are expected from phenomenological thermodynamics.

In order to define the canonical and the grand canonical partition function, one has to confine the particles of the system to lie in a bounded set $\Lambda \subset \mathbb{R}^3$, which we choose to be open. For the confined system to be well defined its Hamiltonian should be self adjoint. This requires that one imposes suitable boundary conditions on the boundary of $\Lambda$. For each particular choice of boundary conditions one obtains a canonical and a grand canonical partition function. In order to study the thermodynamic limit one considers a sequence $\{\Lambda_l\}$ of bounded open domains such that the volume of $\Lambda_l$ tends to infinity as $l \to \infty$. For systems with Dirichlet boundary conditions it was shown in [1] that

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the canonical and grand canonical partition function exist for a large class of limiting sequences \( \{ \Lambda_l \} \). Moreover, the limit is independent of the particular sequence.

In this work we prove that, indeed, the same limit is obtained for systems with Neumann, periodic, or reflecting boundary conditions. We prove our result for limiting sequences which are obtained by scaling a bounded open set, which has a smooth boundary, except for isolated edges and corners. This class of limiting sequences is smaller than the class for which the thermodynamic limit for systems with Dirichlet boundary conditions has been shown to exist. We want to point out that this is only partially technical. For instance, there exist sequences of domains for which the thermodynamic limit of the ground state energy for Dirichlet boundary conditions exists, whereas for Neumann boundary conditions the ground state energy diverges to \(-\infty\). Although such sequences are somewhat pathological, this demonstrates that the independence of boundary conditions for systems composed of electrons and nuclei cannot be considered as trivial. We will also comment on possible more general classes of limiting sequences for which our proof is applicable. For notational simplicity, we only state and prove our results for systems composed of a single species of negatively charged fermions and a single species of positively charged particles being bosons. The results as well as their proofs generalize to multicomponent systems in a straightforward way. We state the main result and present its proof for both: zero temperature and nonnegative temperature. Despite that the latter implies the former, we present that way an independent and technically easier proof for the temperature zero case.

To prove the independence of the boundary conditions we use a sliding technique, which was introduced in [2], and refined in [3]. Thereby, one decomposes the space into simplices. By sliding and rotating the simplices one obtains a lower bound for the Hamiltonian of a large system in terms of Hamiltonians defined on the smaller simplices. Simplices which lie in the interior of the large system have Dirichlet boundary conditions. Whereas simplices on the boundary, i.e., simplices which intersect with the boundary of the large system, are subject to mixed boundary conditions. Using that the many body Coulomb potential can be estimated below by a sum of one body potentials [8], we then show that the thermodynamic quantities in the boundary simplices are bounded. In the thermodynamic limit the sum of all the boundary contributions is proportional to the surface. This is negligible compared to the bulk contribution, which is proportional to the volume.

Our results can be generalized to include tempered interactions (for a definition see e.g. [1]). However, they do not extend to more general long range two body interactions, since our methods are based on the screening property of the Coulomb potential. We want to point out that independence of boundary conditions has been studied for systems with hard core interactions (see [4, 5], and references given therein).

The paper is organized as follows. In Sect. 2 we introduce the model and state the results. In sect. 3 we present the proofs.

2. Model and Statement of Results

We shall first recall the definition of Dirichlet and Neumann boundary conditions [6]. Let \( \Lambda \) be a bounded open set in \( \mathbb{R}^3 \). The Dirichlet Laplacian for \( \Lambda \), \( -\Delta^D_\Lambda \), is the unique self-adjoint operator on \( L^2(\Lambda) \) whose quadratic form is the closure of the form

\[
\phi \mapsto \int_\Lambda |\nabla \phi|^2 \, dx
\]