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The Thermodynamic Limit for a Crystal

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Abstract. Consider a crystal with nucleii fixed at the lattice points in $\Omega \subset \mathbb{R}^3$, interacting by Coulomb forces with quantized electrons in Ω. We prove that the pressure tends to a limit as Ω grows infinitely large.

0. Introduction

A natural model for electrons in a crystal is as follows. We place a nucleus of charge $+1$ at each lattice point in a box $\Omega \subseteq \mathbb{R}^3$. The basic Hamiltonian for N quantized electrons $x_1, \ldots, x_N$ in Ω is

$$H_{N,\Omega} = -\Delta_x + \sum_{j<k} |x_j - x_k|^{-1} + \sum_{j<k} |y_j - y_k|^{-1} - \sum_{j,k} |x_j - y_k|^{-1}$$

with Dirichlet boundary conditions on $\Omega \times \cdots \times \Omega$. Here $y_1 \ldots y_M$ are the nucleii, and $H_{N,\Omega}$ acts on antisymmetric wave functions $\psi(x_1 \ldots x_N)$. If the electrons have temperature β^{-1} and chemical potential μ/β, then up to trivial factors the pressure is given by

$$F = (\mathrm{Vol}\,\Omega)^{-1} \ln\left[\sum_N e^{\mu N} \,\mathrm{Trace}\, e^{-\beta H_{N,\Omega}}\right].$$

The purpose of this paper is to prove that F tends to a limit as the volume of Ω tends to infinity. This is called existence of the thermodynamic limit. See Sect. 2 for the precise statement of our result. The problem of the thermodynamic limit for crystals was posed by Lebowitz and Lieb, following their basic work [1] on real matter, with electrons and nucleii all quantized. Since a crystal is not rotationally symmetric, the method of [1] doesn't work here.

Of course one wants to allow periodic arrangements of nucleii more general than just charge $+1$ at each lattice point; also, we should introduce spin into our wave functions. These refinements can be easily incorporated into our proof. For that matter, it is enough to suppose that the placement of nucleii is asymptotically periodic; and our electrons could be Bosons (or even classical particles provided the nucleii have hard cores).

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