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The van der Waals Limit for Classical Systems. I. A Variational Principle

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Abstract. We consider the thermodynamic pressure $p(\mu, \gamma)$ of a classical system of particles with the two-body interaction potential $q(\mathbf{r}) + \gamma^\nu K(\gamma \mathbf{r})$, where ν is the number of space dimensions, γ is a positive parameter, and μ is the chemical potential. The temperature is not shown in the notation. We prove rigorously, for hard-core potentials $q(\mathbf{r})$ and for a very general class of functions $K(\mathbf{s})$, that the limit $\gamma \to 0$ of the pressure $p(\mu, \gamma)$ exists and is given by

$$\sup_{n \in \mathscr{R}} \lim_{|D| \to \infty} \frac{1}{|D|}\left[\int_D d\mathbf{y}\{\mu n(\mathbf{y}) - a^0[n(\mathbf{y})]\} - \frac{1}{2}\int_D d\mathbf{y} \int_D d\mathbf{y}' n(\mathbf{y}) n(\mathbf{y}') K(\mathbf{y} - \mathbf{y}')\right]$$

where the limit and the supremum can be interchanged. Here $\mathscr{R}$ is a certain class of non-negative, Riemann integrable functions, D is a cube of volume $|D|$, and $a^0(\varrho)$ is the free energy density of a system with $K = 0$ and density ϱ. A similar result is proved for the free energy.

I. Introduction

Many authors have considered the equilibrium statistical mechanics of a system of identical particles which have a two-body interaction potential of the form

$$v(\mathbf{r}, \gamma) = q(\mathbf{r}) + \gamma^\nu K(\gamma \mathbf{r}) \tag{1.1}$$

where $\mathbf{r}$ is the vector distance between a pair of particles, γ is a positive parameter and ν is the number of dimensions. The function $q(\mathbf{r})$ is called the *short range or reference potential* and the term $\gamma^\nu K(\gamma \mathbf{r})$ is called the *long range or Kac potential*, whose range is proportional to γ^{-1}. Some of these authors [1–4] have considered the limiting values of the thermodynamic functions and correlation functions in the limit $\gamma \to 0$; others [3, 5–7] have derived expansions of these functions in powers of γ. We shall be dealing with the former problem. In particular, we shall generalize the results of Lebowitz and Penrose [4] (henceforth referred to as LP) to a wider class of Kac potentials. Both the paper of LP and the present one are motivated to some extent by the work of van Kampen [8].