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The van der Waals Limit for Classical Systems

III. Deviation from the van der Waals-Maxwell Theory

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Abstract. We examine the limiting free energy density $a(\varrho, 0+) \equiv \lim_{\gamma \to 0} a(\varrho, \gamma)$ of a classical system of particles with the two-body potential $q(\mathbf{r}) + \gamma^\nu K(\gamma \mathbf{r})$, at density ϱ in ν dimensions. Starting from a variational formula for $a(\varrho, 0+)$, obtained in Part I of these papers, we obtain a new upper bound on $a(\varrho, 0+)$ given by

$$a(\varrho, 0+) \leqq CE\{ME[a^0(\varrho) + \tfrac{1}{4}\tilde{K}_{\min}\varrho^2] + (\tfrac{1}{2}\alpha - \tfrac{1}{4}\tilde{K}_{\min})\varrho^2\}.$$

Here MEf, called the mid-point envelope of f, is defined for any function f by

$$MEf(\varrho) \equiv \inf_h \tfrac{1}{2}[f(\varrho + h) + f(\varrho - h)];$$

CEf, called the convex envelope of f, is defined for any f as the maximal convex function not exceeding f; also $\alpha \equiv \int d\mathbf{s} K(\mathbf{s})$ and $\tilde{K}_{\min}$ is the minimum of the Fourier transform of K, while $a^0(\varrho)$ is the free energy density for $K = 0$.

For the class of functions K such that $\tilde{K}_{\min} < 0$ and $\tilde{K}_{\min} < 2\alpha$, we deduce from this upper bound that $a(\varrho, 0+) < CE[a^0(\varrho) + \frac{1}{2}\alpha\varrho^2]$ for all values of ϱ where $a^0(\varrho) + \frac{1}{2}\alpha\varrho^2$ differs from its convex envelope, or where $a^0(\varrho) + \frac{1}{4}\tilde{K}_{\min}\varrho^2$ differs from its mid-point envelope. Consequently, the generalized van der Waals equation

$$a(\varrho, 0+) = CE[a^0(\varrho) + \tfrac{1}{2}\alpha\varrho^2]$$

does not apply in this case. We prove that in a certain sense the local density is non-uniform over distances of order γ^{-1} in this case, and infer that this density is periodic.

We also give a simpler derivation of other bounds on $a(\varrho, 0+)$ obtained by Lebowitz and Penrose.

I. Introduction

Following the work of Kac, Uhlenbeck, and Hemmer [1] and van Kampen [2] on the van der Waals equation, Lebowitz and Penrose [3] (henceforth referred to as LP) considered the pressure of a ν-dimensional system of particles with the two-body potential

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