Commun. math. Phys. 16, 231—237 (1970)

The van der Waals Limit for Classical Systems

II. Existence and Continuity of the Canonical Pressure

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Received September 10, 1969

Abstract. For a ν-dimensional system of particles with the two-body potential $q(\boldsymbol{r}) + \gamma^\nu K(\gamma \boldsymbol{r})$ and density ϱ, it is proved under fairly weak conditions on q and K that the canonical pressure $\pi(\varrho, \gamma)$ and chemical potential $\mu(\varrho, \gamma)$ tend to definite limits when $\gamma \to 0$. The limiting functions are absolutely continuous and are given in terms of the derivative of the limiting free energy density $a(\varrho, 0+) \equiv \lim_{\gamma \to 0} a(\varrho, \gamma)$ which was found in Part I.

I. Introduction

In Part I of these papers [1] we considered the free energy density $a(\varrho, \gamma)$ of a ν-dimensional system of particles with the two-body potential

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

and density ϱ. (We assume there is no external field in the present paper). Under fairly weak conditions on q and K we proved that the *van der Waals limit* $a(\varrho, 0+) \equiv \lim_{\gamma \to 0} a(\varrho, \gamma)$ exists and is given by a variational formula.

In the present paper we consider the canonical chemical potential

$$\mu(\varrho, \gamma) \equiv \frac{\partial}{\partial \varrho} a(\varrho, \gamma) \tag{1.2}$$

and the canonical pressure

$$\pi(\varrho, \gamma) \equiv \left(\varrho \frac{\partial}{\partial \varrho} - 1\right) a(\varrho, \gamma) \tag{1.3}$$

for the same system. The existence of these functions was proved by Dobrushin and Minlos [2] (see also [3]). We prove that *their van der Waals limits*

$$\mu(\varrho, 0+) \equiv \lim_{\gamma \to 0} \mu(\varrho, \gamma), \tag{1.4}$$

$$\pi(\varrho, 0+) \equiv \lim_{\gamma \to 0} \pi(\varrho, \gamma) \tag{1.5}$$

exist, are absolutely continuous functions of ϱ (and hence differentiable almost everywhere [4]*), and are given by*

$$\mu(\varrho, 0+) = \frac{\partial}{\partial \varrho} a(\varrho, 0+), \tag{1.6}$$

$$\pi(\varrho, 0+) = \left(\varrho \frac{\partial}{\partial \varrho} - 1\right) a(\varrho, 0+). \tag{1.7}$$

The results (1.6 and 7) mean that the limit $\gamma \to 0$ and the derivative $\partial/\partial\varrho$ of $a(\varrho, \gamma)$ can be interchanged, and that $\mu(\varrho, 0+)$ can be calculated in principle from the variational formula for $a(\varrho, 0+)$ given in Part I.

Our method consists of proving firstly that $a(\varrho, 0+)$ is differentiable. To prove this we note that $a(\varrho, 0+)$ is convex, as shown in Part I, and hence its left and right hand derivatives, denoted by $\partial_- a(\varrho, 0+)$ and $\partial_+ a(\varrho, 0+)$ respectively, exist and satisfy [4]

$$\partial_- a(\varrho, 0+) \leqq \partial_+ a(\varrho, 0+). \tag{1.8}$$

In Section III we complete the proof by showing that $\partial_+ a(\varrho, 0+) \leqq \partial_- a(\varrho, 0+)$, using an inequality obtained in Section II. Secondly, we prove in Section IV that (1.6 and 7) hold.

The conditions to be satisfied by q and K are, as in Part I,

$$q(\boldsymbol{r}) = q(-\boldsymbol{r}), \qquad K(\boldsymbol{s}) = K(-\boldsymbol{s}), \tag{1.9}$$

$$\left.\begin{array}{l} q(\boldsymbol{r}) = \infty \quad \text{for} \quad |\boldsymbol{r}| < r_0 \text{ (hard core condition),} \\ |q(\boldsymbol{r})| < A|\boldsymbol{r}|^{-\nu-\varepsilon} \quad \text{for} \quad |\boldsymbol{r}| \geqq r_0, \\ q \text{ is measurable,} \end{array}\right\} \tag{1.10}$$

$|K(\boldsymbol{s})| < k(|\boldsymbol{s}|) < \bar{K}$ for all $\boldsymbol{s}$, where $k(t)$ is a positive non-increasing function such that $\int d\boldsymbol{s}\, k(|\boldsymbol{s}|) < \infty$, and K is Riemann integrable on any bounded region of ν-dimensional space. (1.11)

Here A, $\bar{K}$, r_0 and ε are positive constants.

II. Inequality for $a(\varrho, \gamma)$

To obtain a suitable inequality for $a(\varrho, \gamma)$ we use the result (3.23) of Dobrushin and Minlos [2]. Let $Z(N, \Omega, \gamma)$ be the partition function (for details see [1]) for N particles in a cube Ω with the two-body potential (1.1), and let N_1 and N_2 be positive integers that do not exceed the maximum value of N for which $Z(N, \Omega, \gamma)$ is defined. Then, with a slight modification[1], their result states that for $N_1 < N_2$

$$N_1\left(\frac{Z(N_1)}{Z(N_1-1)}+C'\right) \leqq N_2\left(\frac{Z(N_2)}{Z(N_2-1)}+C'\right) \tag{2.1}$$

where

$$C'(\gamma) \equiv \Lambda^{-\nu} \exp[2\beta\Phi' + 2\beta\Psi'(\gamma)] \int d\boldsymbol{r}(1-\exp[-\beta q_+(\boldsymbol{r}) - \beta\gamma^\nu K_+(\gamma\boldsymbol{r})]) \tag{2.2}$$

with $q_+(\boldsymbol{r}) \equiv \max(q(\boldsymbol{r}), 0)$ and $K_+(s) \equiv \max(K(s), 0)$. The dependence of Z on Ω and γ, and of C' on γ in (2.1) is omitted from the notation. Here Λ is the thermal wavelength [1], while $-2\Phi'$ and $-2\Psi'$ are lower bounds on the contributions to the potential energy, due to $q(\boldsymbol{r})$ and $\gamma^\nu K(\gamma \boldsymbol{r})$ respectively, of a single particle interacting with any number of other particles. The existence of these lower bounds is a consequence of the conditions (1.9 to 11) (compare [5]).

From (2.1) we shall deduce the new inequality

$$N_1\left[\left(\frac{Z(N)}{Z(N_1)}\right)^{1/(N-N_1)}+C'\right] \leqq N_2\left[\left(\frac{Z(N_2)}{Z(N)}\right)^{1/(N_2-N)}+C'\right] \tag{2.3}$$

for $N_1 < N < N_2$. To prove this we firstly use (2.1), with N' replacing N_1 and N replacing N_2, to obtain

$$\begin{aligned} 0 < \frac{Z(N)}{Z(N_1)} &= \prod_{N'=N_1+1}^{N} \frac{Z(N')}{Z(N'-1)} \\ &\leqq \prod_{N'=N_1+1}^{N} \left[\frac{N}{N'}\left(\frac{Z(N)}{Z(N-1)}+C'\right)-C'\right] \qquad (2.4) \\ &\leqq \left[\frac{N}{N_1}\left(\frac{Z(N)}{Z(N-1)}+C'\right)-C'\right]^{N-N_1}. \end{aligned}$$

This gives

$$N_1\left[\left(\frac{Z(N)}{Z(N_1)}\right)^{1/(N-N_1)}+C'\right] \leqq N\left(\frac{Z(N)}{Z(N-1)}+C'\right). \tag{2.5}$$

Secondly, we use (2.1) again to obtain for $N < N' \leqq N_2$

$$\frac{Z(N')}{Z(N'-1)} \geqq \frac{N}{N_2}\left(\frac{Z(N)}{Z(N-1)}+C'\right)-C'. \tag{2.6}$$

Suppose, for a given N, that N_2 is so small that the right side of (2.6) is non-negative. We then have, as in (2.4),

$$\frac{Z(N_2)}{Z(N)} = \prod_{N'=N+1}^{N_2} \frac{Z(N')}{Z(N'-1)} \geqq \left[\frac{N}{N_2}\left(\frac{Z(N)}{Z(N-1)}+C'\right)-C'\right]^{N_2-N} \tag{2.7}$$

[1] Replace $|\psi_{N-1}-\psi_N|$ by $\max(\psi_{N-1}-\psi_N, 0)$ in Eq. (3.16) of Dobrushin and Minlos. See also [3].

which gives

$$N\left(\frac{Z(N)}{Z(N-1)}+C'\right) \leqq N_2\left[\left(\frac{Z(N_2)}{Z(N)}\right)^{1/(N_2-N)}+C'\right]. \tag{2.8}$$

On the other hand, if N_2 is such that the right side of (2.6) is negative then (2.8) still holds because $[Z(N_2)/Z(N)]^{1/(N_2-N)}$ is positive. Combining (2.5) and (2.8) gives the desired inequality (2.3).

To obtain an inequality for the free energy density

$$a(\varrho,\gamma) \equiv -\lim_{|\Omega|\to\infty} \frac{1}{\beta|\Omega|} \log Z(\varrho|\Omega|,\Omega,\gamma) \tag{2.9}$$

where $|\Omega|$ is the volume of Ω, we divide both sides of (2.3) by $|\Omega|$ and take the thermodynamic limit $|\Omega|\to\infty$, with $N/|\Omega|\to\varrho$ and $N_i/|\Omega|\to\varrho_i$. This immediately gives

$$\begin{aligned}\varrho_1&\left[C'(\gamma)+\exp\left(\frac{\beta a(\varrho_1,\gamma)-\beta a(\varrho,\gamma)}{\varrho-\varrho_1}\right)\right] \\ &\leqq \varrho_2\left[C'(\gamma)+\exp\left(\frac{\beta a(\varrho,\gamma)-\beta a(\varrho_2,\gamma)}{\varrho_2-\varrho}\right)\right]\end{aligned} \tag{2.10}$$

for all γ and all ϱ, ϱ_1 and ϱ_2 that satisfy $0 \leqq \varrho_1 < \varrho < \varrho_2 < \varrho_c$, where ϱ_c is the maximum density permitted by q.

Before proceeding with the main part of the proof, we note that since $a(\varrho,\gamma)$ is convex [3] in ϱ, it satisfies an inequality like (1.8). Also, taking the limits $\varrho_1\to\varrho$ and $\varrho_2\to\varrho$ of (2.10) gives $\partial_- a(\varrho,\gamma) \geqq \partial_+ a(\varrho,\gamma)$, which proves that $a(\varrho,\gamma)$ is differentiable. The same result was obtained in [2] by a slightly different method.

III. Differentiability of $a(\varrho, 0+)$

In this section we prove that $a(\varrho, 0+)$ is differentiable by considering the limit $\gamma\to 0$ of (2.10). We note that (2.10) still holds if C' is replaced by an upper bound, C say, on C'. To find a suitable upper bound we note that $q_+ \geqq 0$, $K_+ \geqq 0$ and $1-e^{-x} \leqq x$ for all x, which gives

$$\begin{aligned}1-e^{-\beta(q_+ + \gamma^\nu K_+)} &= (1-e^{-\beta q_+}) + e^{-\beta q_+}(1-e^{-\beta\gamma^\nu K_+}) \\ &\leqq (1-e^{-\beta q_+}) + \beta\gamma^\nu K_+ .\end{aligned} \tag{3.1}$$

It follows that

$$\int d\boldsymbol{r}(1-\exp[-\beta q_+(\boldsymbol{r}) - \beta\gamma^\nu K_+(\gamma\boldsymbol{r})]) \leqq B + \beta\alpha_+ \tag{3.2}$$

where

$$B \equiv \int d\boldsymbol{r}(1-\exp[-\beta q_+(\boldsymbol{r})]) \tag{3.3}$$

and

$$\alpha_+ \equiv \int ds\, K_+(s)\,. \tag{3.4}$$

Also, let us choose

$$\Psi'(\gamma) \equiv -\frac{1}{2} \inf_{r_1, r_2, \ldots} \sum_{a=1}^{\infty} \gamma^\nu K(\gamma r_a) \tag{3.5}$$

the infimum being over r_a's that are subject to $|r_a - r_b| \geqq r_0$ for all $a \neq b$, where r_0 is the hard core diameter of q. To obtain an upper bound on Ψ' we consider, as in Part I, an infinite lattice of identical cubes $\omega_1, \omega_2, \ldots$ of volume ω filling ν-dimensional space. Putting

$$K_i \equiv \inf_{r \in \omega_i} K_-(\gamma r) \tag{3.6}$$

where $K_-(s) \equiv \min(K(s), 0)$, we obtain

$$\sum_{a=1}^{\infty} K(\gamma r_a) \geqq \sum_{i=1}^{\infty} N_i K_i \tag{3.7}$$

where N_i is the number of particles whose centres are contained in ω_i for a given $(r_1, r_2, \ldots)$. As shown in [6], N_i cannot exceed $\varrho_c(\omega^{1/\nu} + 2r_0)^\nu$. Hence, from (3.5) and (3.7), we have for all γ and ω

$$\Psi'(\gamma) \leqq \Psi(\gamma, \omega) \equiv -\frac{1}{2} \varrho_c (1 + 2r_0 \omega^{-1/\nu})^\nu \sum_{i=1}^{\infty} (\gamma^\nu \omega) K_i\,. \tag{3.8}$$

Together with (3.2) and (2.2) this gives for all γ and ω

$$C'(\gamma) \leqq C(\gamma, \omega) \equiv \Lambda^{-\nu}(B + \beta\alpha_+) e^{2\beta[\Phi' + \Psi(\gamma,\omega)]}\,. \tag{3.9}$$

Now consider the limit operations $\gamma \to 0$ followed by $\omega \to \infty$ applied to $C(\gamma, \omega)$. The conditions (1.11) imply [7] that

$$\lim_{\omega \to \infty} \lim_{\gamma \to 0} \Psi(\gamma, \omega) = -\frac{1}{2} \varrho_c \alpha_- \tag{3.10}$$

where

$$\alpha_- \equiv \int ds\, K_-(s)\,. \tag{3.11}$$

This, together with (3.9) implies that

$$C(0+) \equiv \lim_{\omega \to \infty} \lim_{\gamma \to 0} C(\gamma, \omega) = \Lambda^{-\nu}(B + \beta\alpha_+) e^{\beta(2\Phi' - \varrho_c \alpha_-)}\,. \tag{3.12}$$

The expression on the right side simplifies in an obvious way if K is either non-positive or non-negative.

Since the limit (3.12) exists, we can replace $C'(\gamma)$ by $C(\gamma, \omega)$ in (2.10), and take the limits $\gamma \to 0$ followed by $\omega \to \infty$ in the resulting inequality.

This yields [2]

$$\varrho_1\left[C(0+)+\exp\left(\frac{\beta a(\varrho_1,0+)-\beta a(\varrho,0+)}{\varrho-\varrho_1}\right)\right] \leqq \varrho_2\left[C(0+)+\exp\left(\frac{\beta a(\varrho,0+)-\beta a(\varrho_2,0+)}{\varrho_2-\varrho}\right)\right] \tag{3.13}$$

for all ϱ, ϱ_1 and ϱ_2 that satisfy $0\leqq\varrho_1<\varrho<\varrho_2<\varrho_c$.

Finally, taking the limits $\varrho_1\to\varrho$ and $\varrho_2\to\varrho$ gives

$$\partial_- a(\varrho,0+)\geqq\partial_+ a(\varrho,0+) \tag{3.14}$$

which together with (1.8) implies that $a(\varrho,0+)$ is differentiable.

IV. Existence and Continuity of $\mu(\varrho, 0+)$ and $\pi(\varrho, 0+)$

The existence of $\mu(\varrho,0+)$ and the statement (1.6) follow from the differentiability of $a(\varrho,0+)$ and the inequality

$$\partial_- a(\varrho,0+)\leqq\liminf_{\gamma\to 0}\mu(\varrho,\gamma)\leqq\limsup_{\gamma\to 0}\mu(\varrho,\gamma)\leqq\partial_+ a(\varrho,0+) \tag{4.1}$$

which in turn follows from the convexity of $a(\varrho,\gamma)$, (see Eq. (6.5) of Ref. [7]). The existence of $\pi(\varrho,0+)$, and also the statement (1.7), follow from (1.3), (1.5), and (1.6).

The prove the absolute continuity of $\mu(\varrho,0+)$ and $\pi(\varrho,0+)$ we use the Lipschitz condition

$$0\leqq\pi(\varrho_2,\gamma)-\pi(\varrho_1,\gamma)\leqq(\varrho_2-\varrho_1)\,\beta^{-1}[1+C'(\gamma)e^{\beta\mu(\varrho,\gamma)}] \tag{4.2}$$

for all γ and all ϱ_1, ϱ_2 and ϱ that satisfy $0\leqq\varrho_1<\varrho<\varrho_2<\varrho_c$. The first inequality in (4.2) states that $\pi(\varrho,\gamma)$ is non-decreasing [3] in ϱ, while the second inequality is due to Penrose [3] and can be deduced from (2.1). Again we can replace $C'(\gamma)$ by $C(\gamma,\omega)$ in (4.2) and take the limits $\gamma\to 0$ and $\omega\to\infty$. This gives a Lipschitz condition on $\pi(\varrho,0+)$ which proves [4] that it, and hence $\mu(\varrho,0+)$, are absolutely continuous.

As a corollary, we note that when $\partial\pi(\varrho,0+)/\partial\varrho$ exists it satisfies

$$0\leqq\frac{\partial}{\partial\varrho}\pi(\varrho,0+)\leqq\beta^{-1}[1+C(0+)e^{\beta\mu(\varrho,0+)}] \tag{4.3}$$

where $C(0+)$ is given by (3.12). This derivative does not always exist: for example, it has discontinuities in the special case $K\leqq 0$ considered by Lebowitz and Penrose [7, 1].

Using the methods of Dobrushin and Minlos [2], it may be possible to extend our results to cover the case where q does not have a hard

[2] We have tried, without success, to deduce (3.13) directly from the variational formula for $a(\varrho,0+)$ given in Part I.

core, provided that the existence of $a(\varrho, 0+)$ can also be proved in this case.

Our results can be extended to include an external potential $\psi(\gamma \boldsymbol{x})$, as in [1], where $\psi(\boldsymbol{y})$ is periodic, Riemann integrable, and satisfies $|\psi(\boldsymbol{y})| < \overline{\psi}$, a constant, for all $\boldsymbol{y}$. To do this we need only replace C' everywhere by $C' e^{\beta \overline{\psi}}$.

Acknowledgement. We gratefully acknowledge financial support for D. J. Gates from 'The Royal Commission for the Exhibition of 1851'.

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