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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

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

and showed that in the limit $\gamma \to 0$ this pressure is given, for a certain class of functions K, by a generalization of the van der Waals equation together with the Maxwell construction. In the present paper we prove that, for a different class of functions K, this equation does *not* hold.

Our method is based on the results of Part I of this series of papers [4]. We there proved that the free energy density $a(\varrho, T, \gamma)$ of a classical system of particles, with the two-body potential (1.1) at temperature T and density ϱ, tends to a definite limit when $\gamma \to 0$ (the *van der Waals limit*), provided that both q and K satisfy fairly weak tempering conditions and that q has a hard core. As before $q(\mathbf{r})$ is called the *reference potential* and $\gamma^\nu K(\gamma \mathbf{r})$ the *Kac potential*. We proved further that

$$a(\varrho, T, 0+) \equiv \lim_{\gamma \to 0} a(\varrho, T, \gamma) = \inf_{n \in \mathscr{C}(\varrho)} G(n, T) \tag{1.2}$$

where the functional G is given by

$$G(n, T) = \frac{1}{|\Gamma|} \int_\Gamma d\mathbf{y} \left\{ a^0[n(\mathbf{y}), T] + \tfrac{1}{2} n(\mathbf{y}) \int d\mathbf{y}' n(\mathbf{y}') K(\mathbf{y} - \mathbf{y}') \right\} \tag{1.3}$$

the integral with respect to $\mathbf{y}'$ being over all of ν-dimensional space. Here $\mathscr{C}(\varrho)$ is the class of functions n that (i) are bounded by 0 and ϱ_c (the maximum density permitted by q), (ii) are Riemann integrable over any bounded region, (iii) are periodic, and (iv) have space average ϱ, i.e.

$$\frac{1}{|\Gamma|} \int_\Gamma d\mathbf{y}\, n(\mathbf{y}) = \varrho\,. \tag{1.4}$$

The region Γ (which depends on n) is the unit cell of n and has volume $|\Gamma|$. The function $a^0(\varrho, T)$ is the free energy density corresponding to a system with the two-body potential $q(\mathbf{r})$, called the *reference system*.

We shall use (1.2 and 3) to obtain an upper bound on $a(\varrho, T, 0+)$, but first let us consider the bounds already obtained by LP. They showed that

$$\begin{aligned} CE[a^0(\varrho, T) + \tfrac{1}{2}\tilde{K}_{\min}\varrho^2] + \tfrac{1}{2}(\alpha - \tilde{K}_{\min})\varrho^2 &\leqq a(\varrho, T, 0+) \\ &\leqq CE[a^0(\varrho, T) + \tfrac{1}{2}\alpha\varrho^2] \end{aligned} \tag{1.5}$$

where $\tilde{K}_{\min}$ is the minimum of the Fourier transform

$$\tilde{K}(\mathbf{p}) \equiv \int d\mathbf{s}\, e^{2\pi i \mathbf{p}\cdot\mathbf{s}} K(\mathbf{s})\,, \tag{1.6}$$

$\alpha \equiv \int d\mathbf{s}\, K(\mathbf{s}) = \tilde{K}(0)$, and CEf, called the *convex envelope* of f, is defined for arbitrary f as the maximal convex function not exceeding f. These bounds coincide in the following cases:

(a) If $\tilde{K}(\mathbf{p}) \geqq 0$ for all $\mathbf{p}$ (so that $\alpha \geqq 0$) then

$$a(\varrho, T, 0+) = a^0(\varrho, T) + \tfrac{1}{2}\alpha\varrho^2 \tag{1.7}$$

for all ϱ and T.

(b) If[1] $\tilde{K}(\mathbf{p}) \geqq \tilde{K}(0)$ for all $\mathbf{p}$ (of which a special case is $K(\mathbf{s}) \leqq 0$ for all $\mathbf{s}$) then $\tilde{K}_{\min} = \alpha$ and hence

$$a(\varrho, T, 0+) = CE[a^0(\varrho, T) + \tfrac{1}{2}\alpha\varrho^2] \quad \text{for all } \varrho \text{ and } T. \tag{1.8}$$

The canonical pressure corresponding to (1.8) is given by a generalization of the van der Waals-Maxwell equation of state.

(c) For a general K, (1.7) holds for values of ϱ and T where $a^0 + \frac{1}{2}\tilde{K}_{\min}\varrho^2$ coincides with its convex envelope. One expects for any a^0, and can show for certain cases of a^0, that this happens at least when $\varrho \approx 0$ and when $\varrho \approx \varrho_c$.

(d) If a^0 shows no first order phase transition and

$$T^{-1}\,\partial^2 a^0(\varrho, T)/\partial\varrho^2 \geqq C$$

for all ϱ and T, where C is a positive constant, then (1.7) holds for all ϱ provided that

$$T \geqq |\tilde{K}_{\min}|/C\,. \tag{1.9}$$

To prove this, we merely note that $a^0 + \frac{1}{2}\tilde{K}_{\min}\varrho^2$ is convex when (1.9) holds. As an example, when q corresponds to a one-dimensional system of hard rods of length r_0 we find that $C = 27k/4r_0$ where k is Boltzmann's constant.

The bounds on $a(\varrho, T, 0+)$ given by (1.5) do not exclude the possibility that (1.8) might hold for all functions K and for all ϱ and T. To show that this is not so, we obtain a stronger upper bound on $a(\varrho, T, 0+)$ which enables us to find some conditions under which

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

II. Stronger Upper Bound on the Free Energy

This section is devoted to obtaining the above mentioned upper bound on $a(\varrho, 0+)$ (dependence on T is henceforth omitted from the notation). Our method consists of choosing judiciously a function $n \in \mathscr{C}(\varrho)$, noting that $a(\varrho, 0+) \leqq G(n)$, and finding an upper bound on $G(n)$ for this function n.

As a first choice one might try $n = \varrho$, which clearly belongs to $\mathscr{C}(\varrho)$, and which by (1.2) gives $a(\varrho, 0+) \leqq G(\varrho) = a^0(\varrho) + \frac{1}{2}\alpha\varrho^2$. Since $a(\varrho, 0+)$ is convex [4], it follows that $a(\varrho, 0+) \leqq CE[a^0(\varrho) + \frac{1}{2}\alpha\varrho^2]$. This is just the result (1.5) of LP, but here it is an almost trivial consequence of the variational formula.

[1] This implies $\alpha \leqq 0$ since $\tilde{K}(\mathbf{p}) \to 0$ as $|\mathbf{p}| \to \infty$.

To obtain a stronger upper bound, let $\mathbf{p}_0$ be a value of $\mathbf{p}$ where $\tilde{K}(\mathbf{p})$ attains[2] its minimum, i.e. $\tilde{K}(\mathbf{p}_0)=\tilde{K}_{\min}$. Now let us choose

$$n(\mathbf{y})=\varrho+h\sin(2\pi\mathbf{p}_0\cdot\mathbf{y}) \tag{2.1}$$

with h a positive constant and $0\leqq\varrho\pm h\leqq\varrho_c$ for a given ϱ. Hence we have $n\in\mathscr{C}(\varrho)$. In this case the unit cell Γ of n has length $|\mathbf{p}_0|^{-1}$ in the $\mathbf{p}_0$ direction, while its other dimensions are arbitrary. Our choice of n is motivated by the conjecture of LP that spatial ordering may occur; the sine function is chosen so that the calculations are simple; and the period is chosen so as to give the best possible upper bound for functions of this form.

To obtain an upper bound on $G(n)$, defined by (1.3), we first find an upper bound on its quadratic term

$$I(n)\equiv\frac{1}{|\Gamma|}\int_\Gamma d\mathbf{y}\int d\mathbf{y}'\,K(\mathbf{y}-\mathbf{y}')\,n(\mathbf{y})\,n(\mathbf{y}'). \tag{2.2}$$

This can be written as

$$I(n)=\sum_{\mathbf{p}\in V_\Gamma}\tilde{K}(\mathbf{p})\,|n(\mathbf{p})|^2 \tag{2.3}$$

where V_Γ is the set of all vectors that connect points in the reciprocal lattice of the unit cell Γ, while $\tilde{K}$ is defined by (1.6) and $\tilde{n}$ by

$$\tilde{n}(\mathbf{p})\equiv\frac{1}{|\Gamma|}\int_\Gamma d\mathbf{y}\,n(\mathbf{y})\,e^{2\pi i\mathbf{p}\cdot\mathbf{y}}. \tag{2.4}$$

For the choice (2.1) of n we obtain

$$\tilde{n}(\mathbf{p})=\begin{cases}\varrho & \text{for}\quad \mathbf{p}=0,\\ \pm\tfrac{1}{2}ih & \text{for}\quad \mathbf{p}=\pm\mathbf{p}_0,\\ 0 & \text{otherwise}.\end{cases} \tag{2.5}$$

Hence from (2.3) we have

$$\begin{aligned}I(n)&=\tilde{K}(0)\varrho^2+2\tilde{K}(\mathbf{p}_0)\,(h/2)^2\\ &=\alpha\varrho^2+\tfrac{1}{2}\tilde{K}_{\min}h^2.\end{aligned} \tag{2.6}$$

Next we find an upper bound on the integral involving a^0 in the functional $G(n)$. Since $a^0(\varrho)$ is convex we have, for all ϱ' in the interval $[\varrho-h,\varrho+h]$,

$$a^0(\varrho')\leqq\frac{\varrho'-\varrho+h}{2h}\,a^0(\varrho+h)+\frac{\varrho+h-\varrho'}{2h}\,a^0(\varrho-h). \tag{2.7}$$

[2] The minimum is attained because $\tilde{K}(\mathbf{p})$ is continuous [3].

But (2.1) implies that $\varrho - h \leqq n(\mathbf{y}) \leqq \varrho + h$ for all $\mathbf{y}$, and hence

$$\begin{aligned}\frac{1}{|\Gamma|}\int_\Gamma d\mathbf{y}\, a^0[n(\mathbf{y})] &\leqq \frac{a^0(\varrho+h)}{2h|\Gamma|}\int_\Gamma d\mathbf{y}[n(\mathbf{y})-\varrho+h] \\ &\quad + \frac{a^0(\varrho-h)}{2h|\Gamma|}\int_\Gamma d\mathbf{y}[\varrho+h-n(\mathbf{y})] \\ &= \tfrac{1}{2}a^0(\varrho+h)+\tfrac{1}{2}a^0(\varrho-h)\end{aligned} \tag{2.8}$$

Combining (2.6) with (2.8) and (1.3) gives an upper bound on $a(\varrho, 0+)$ which is conveniently expressed in the form

$$\begin{aligned}a(\varrho,0+) &\leqq \tfrac{1}{2}\{a^0(\varrho+h)+a^0(\varrho-h)+\tfrac{1}{4}\tilde{K}_{\min}[(\varrho+h)^2+(\varrho-h)^2]\} \\ &\quad + (\tfrac{1}{2}\alpha - \tfrac{1}{4}\tilde{K}_{\min})\varrho^2 .\end{aligned} \tag{2.9}$$

Because of the arbitrariness of h, we can minimize the right side with respect to h, which gives

$$a(\varrho,0+) \leqq ME[a^0(\varrho)+\tfrac{1}{4}\tilde{K}_{\min}\varrho^2]+(\tfrac{1}{2}\alpha-\tfrac{1}{4}\tilde{K}_{\min})\varrho^2 , \tag{2.10}$$

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

$$MEf(\varrho) \equiv \inf_{h\in D_\varrho} \tfrac{1}{2}[f(\varrho+h)+f(\varrho-h)] , \tag{2.11}$$

where D_ϱ is the set of values of h such that $\varrho - h$ and $\varrho + h$ lie in the domain of f. Since $a(\varrho, 0+)$ is convex [4], we obtain from (2.10) our first main result:

Theorem 1. *If q and K satisfy the conditions of Part I, then*

$$a(\varrho,0+) \leqq CE\{ME[a^0(\varrho)+\tfrac{1}{4}\tilde{K}_{\min}\varrho^2]+(\tfrac{1}{2}\alpha-\tfrac{1}{4}\tilde{K}_{\min})\varrho^2\} . \tag{2.12}$$

We note that this upper is at least as strong as the LP upper bound $CE[a^0+\frac{1}{2}\alpha\varrho^2]$ because, from (2.11), $MEf \leqq f$ for any function f.

III. The Mid-Point Envelope

To proceed further we need to know more about the function MEf defined by (2.11). We shall prove the following lemmas.

Lemma 1. *For any function f,*

$$CEf(\varrho) \leqq MEf(\varrho) \leqq f(\varrho) \quad \textit{for all } \varrho . \tag{3.1}$$

The equalities apply for all ϱ if f is convex.

Lemma 2. *If $CEf < f$ in some bounded open interval, but not at the end points, and ϱ_M is the mid-point of this interval, then*

$$MEf(\varrho_M) = CEf(\varrho_M)\,. \tag{3.2}$$

Lemma 3. *A function f is convex in any interval where it coincides with MEf.*

These lemmas give some guide to the shape of MEf, an example of which is shown in Fig. 1.

To prove Lemma 1, we note that in any interval $[\varrho - h, \varrho + h]$ the graph of CEf, being convex, lies on or below the chord which meets it at $\varrho - h$ and $\varrho + h$. In particular, at the mid-point of this interval we have

$$\begin{aligned} CEf(\varrho) &\leqq \tfrac{1}{2}CEf(\varrho - h) + \tfrac{1}{2}CEf(\varrho + h) \\ &\leqq \tfrac{1}{2}f(\varrho - h) + \tfrac{1}{2}f(\varrho + h)\,, \end{aligned} \tag{3.3}$$

where the second inequality holds because $CEf \leqq f$ for any f. Minimizing the right side of (3.3) over all $h \in D_\varrho$, and using (2.11), gives the first inequality in Lemma 1. The second inequality follows directly from (2.11).

To prove Lemma 2, let ϱ_- and ϱ_+ be the end points of an interval where $CEf < f$ (see Fig. 1). We then have $CEf(\varrho_\pm) = f(\varrho_\pm)$ so that

$$\begin{aligned} CEf(\varrho_M) &= \tfrac{1}{2}[f(\varrho_+) + f(\varrho_-)] \\ &\geqq \inf_h [f(\varrho_M + h) + f(\varrho_M - h)] \\ &= MEf(\varrho_M)\,. \end{aligned} \tag{3.4}$$

This, together with Lemma 1, proves Lemma 2.

To prove Lemma 3, let J be any interval in which f is strictly concave (see [6] p. 75), and let J_ϱ be the set of values of h such that $\varrho \pm h \in J$.

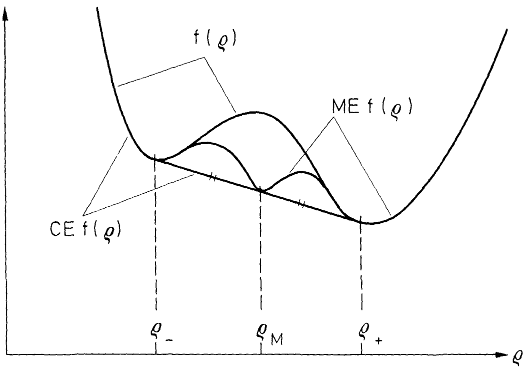

Fig. 1. An example of a function f and its envelopes. The lines marked with a double stroke have equal lengths

Since $J_\varrho \subset D_\varrho$, we have from (2.11)

$$MEf(\varrho) \leqq \underset{J}{ME}f(\varrho) \quad \text{for} \quad \varrho \in J, \tag{3.5}$$

where

$$\underset{J}{ME}f(\varrho) \equiv \inf_{h \in J_\varrho} [f(\varrho + h) + f(\varrho - h)]. \tag{3.6}$$

Let $\underset{J}{CE}f$, called the convex envelope over J of f, be the maximal function which is convex in J, and does not exceed f. Then if ϱ' is the mid-point of J, we have by Lemma 2 and the definition of J

$$\underset{J}{ME}f(\varrho') = \underset{J}{CE}f(\varrho') < f(\varrho'). \tag{3.7}$$

It follows from (3.5 and 7) that $MEf(\varrho') < f(\varrho')$, so that J cannot be a subset of the set of values of ϱ where $MEf = f$; i.e. this latter set has no subinterval in which f is strictly concave. Thus f is convex throughout the set, which proves Lemma 3.

For most functions f, we find that MEf can be found only by numerical methods. The following examples are exceptions which we have found useful:

(i) $ME(\sin\varrho) = -|\sin\varrho|$. (3.8)

(ii) If $f(\varrho)$ is a quartic polynomial in ϱ, whose fourth derivative f_4 (a constant) is positive, then

$$MEf(\varrho) = \begin{cases} f(\varrho) & \text{for all } \varrho \text{ where } f_2(\varrho) \geqq 0, \\ f(\varrho) - \frac{3}{2}[f_2(\varrho)]^2/f_4 & \text{where} \quad f_2(\varrho) \leqq 0, \end{cases} \tag{3.9}$$

where $f_2(\varrho) \equiv \partial^2 f(\varrho)/\partial\varrho^2$. We leave the proofs of (3.8) and (3.9) to the reader.

We require two further lemmas for use in the following section.

Lemma 4. *For any constants A and B and any function f*

$$ME[f(\varrho) + A\varrho + B] = MEf(\varrho) + A\varrho + B \tag{3.10}$$

and

$$CE[f(\varrho) + A\varrho + B] = CEf(\varrho) + A\varrho + B. \tag{3.11}$$

Lemma 5. *For any functions f and g with the same domain*

$$ME(f+g) \geqq MEf + MEg \tag{3.12}$$

and

$$CE(f+g) \geqq CEf + CEg. \tag{3.13}$$

Eq. (3.10) follows directly from (2.11). Eq. (3.11) follows from the fact that CEf can be found by the double tangent construction [3].

To prove (3.12) we note from (2.11) that

$$MEf(\varrho)+MEg(\varrho)\leqq \tfrac{1}{2}[f(\varrho+h)+g(\varrho+h)+f(\varrho-h)+g(\varrho-h)] \tag{3.14}$$

for all h and ϱ such that $\varrho+h$ and $\varrho-h$ are in the domain of f and g. Minimizing the right side with respect to h gives (3.12). To prove (3.13) we use Lemma 1 and obtain

$$CEf+CEg\leqq f+g\,. \tag{3.15}$$

But since the left side is convex, the result (3.13) follows.

IV. Deviation from the van der Waals-Maxwell (vdWM) Theory

In this section we deduce some consequences of Theorem 1. Firstly (Theorem 2) we prove that there is deviation from the vdWM theory under certain conditions, and secondly (Theorem 3) we find some intervals of values of ϱ in which such deviation occurs.

Theorem 2. *If* $\tilde{K}_{\min}<0$ *and* $\tilde{K}_{\min}<2\alpha$, *and the function* $a^0(\varrho,T)+\frac{1}{4}\tilde{K}_{\min}\varrho^2$ *is not convex in* ϱ *(i.e. T is sufficiently low), then there are values of* ϱ *for which*

$$a(\varrho,T,0+)<CE[a^0(\varrho,T)+\tfrac{1}{2}\alpha\varrho^2]\,; \tag{4.1}$$

i.e. the free energy is less than that given by the vdWM theory.

To prove this theorem we need only show that there is one value of ϱ where (4.1) holds. Let us put

$$\lambda\equiv\tfrac{1}{2}\alpha-\tfrac{1}{4}\tilde{K}_{\min}>0 \tag{4.2}$$

and

$$\varphi(\varrho)\equiv a^0(\varrho)+\tfrac{1}{4}\tilde{K}_{\min}\varrho^2\,. \tag{4.3}$$

Since φ is continuous, it follows from the conditions of Theorem 2 that $CE\varphi<\varphi$ in some set of intervals. Let ϱ_M be the mid-point of one such interval, chosen so that $CE\varphi=\varphi$ at the ends of the interval. We shall prove that

$$CE(ME\varphi+\lambda\varrho^2)<CE(\varphi+\lambda\varrho^2)\quad\text{for}\quad \varrho=\varrho_M\,, \tag{4.4}$$

which, together with Theorem 1, proves that (4.1) holds for $\varrho=\varrho_M$.

To prove (4.4) we note that

$$CE(ME\varphi+\lambda\varrho^2)\leqq ME\varphi+\lambda\varrho^2\,, \tag{4.5}$$

and hence from Lemma 2

$$CE(ME\varphi+\lambda\varrho^2)\leqq CE\varphi(\varrho_M)+\lambda\varrho_M^2\quad\text{for}\quad\varrho=\varrho_M\,. \tag{4.6}$$

To proceed further we need

Lemma 6. *With the definitions (4.2 and 3)*

$$CE\varphi + \lambda\varrho^2 < CE(\varphi + \lambda\varrho^2) \tag{4.7}$$

for all values of ϱ where $CE\varphi(\varrho) < \varphi(\varrho)$.

Proof. From Lemma 5 we have

$$CE\varphi \leqq CE(\varphi + \lambda\varrho^2) - \lambda\varrho^2 . \tag{4.8}$$

Let A be some interval in which $CE\varphi < \varphi$, and let $C^1 \dots C^n$ be the sub-intervals (if any) of A in which $CE(\varphi + \lambda\varrho^2) < \varphi + \lambda\varrho^2$. Taking the convex envelope over C^i (defined as in (3.7)) of both sides of (4.8) gives

$$\begin{aligned} CE\varphi &\leqq \underset{C^i}{CE}[CE(\varphi + \lambda\varrho^2) - \lambda\varrho^2] \\ &= CE(\varphi + \lambda\varrho^2) + \underset{C^i}{CE}(-\lambda\varrho^2) , \end{aligned} \tag{4.9}$$

where the equality holds (see Lemma 4) because $CE(\varphi + \lambda\varrho^2)$ is linear for $\varrho \in C^i$. From the graph of $-\lambda\varrho^2$ it is apparent that

$$\underset{C^i}{CE}(-\lambda\varrho^2) < -\lambda\varrho^2 \quad \text{for} \quad \varrho \in C^i , \tag{4.10}$$

which, together with (4.9), shows that (4.7) holds in each C^i. In $A - \sum_{i=1}^{n} C^i$ we have, by the definitions of A and C^i,

$$CE\varphi + \lambda\varrho^2 < \varphi + \lambda\varrho^2 = CE(\varphi + \lambda\varrho^2) . \tag{4.11}$$

Thus (4.7) holds in A, and hence in any interval in which $CE\varphi < \varphi$, which proves Lemma 6.

Since ϱ_M belongs to the set of values of ϱ in which $CE\varphi < \varphi$, it follows that (4.7) holds for $\varrho = \varrho_M$. Combining the result with (4.6) gives (4.4), which proves Theorem 2.

Our next result is

Theorem 3. *Under the conditions of Theorem 2, the set of values of ϱ in which* (4.1) *holds includes (a) those intervals where $a^0(\varrho, T) + \frac{1}{2}\alpha\varrho^2$ differs from its convex envelope, and also (b) those intervals where $a^0(\varrho, T) + \frac{1}{4}\tilde{K}_{\min}\varrho^2$ differs from its mid-point envelope.*

By Lemma 3, the intervals (b) contain those intervals where $a^0 + \frac{1}{4}\tilde{K}_{\min}\varrho^2$ is strictly concave. We note that if $\alpha \geqq 0$ then $a^0 + \frac{1}{2}\alpha\varrho^2$ is convex, so that only intervals of type (b) can occur. If $\alpha < 0$ the intervals (a) are easier to find (because convex envelopes are easier to calculate than mid-point envelopes), but if $|\tilde{K}_{\min}| \gg 2|\alpha|$ then the intervals (b) give a stronger result.

To prove Theorem 3 we refer to (4.2 and 3). Since φ is continuous but not convex, we have $ME\varphi < \varphi$ in some set of intervals $M_1 \dots M_p$ of values of ϱ (i.e. the intervals (b)), and $CE(\varphi + \lambda\varrho^2) < \varphi + \lambda\varrho^2$ in some (possibly empty) set of intervals $C_1 \dots C_q$ (i.e. the intervals (a)). These intervals are open and, since $0 \leqq \varrho \leqq \varrho_c$, are bounded. We shall prove that

$$\begin{aligned}&CE(ME\varphi + \lambda\varrho^2) < CE(\varphi + \lambda\varrho^2)\\&\text{if } \varrho \text{ lies in any of the intervals } M_1 \dots M_p \text{ or } C_1 \dots C_q\,.\end{aligned} \tag{4.12}$$

This together with Theorem 1 implies Theorem 3.

To prove (4.12), we note that the set of all M's and C's can be covered by a set of (possibly intersecting) intervals $B_1 \dots B_r$ each of which is of one of the following types:

(i) The union of an M_i, not contained in any C, with all the C's that intersect it.

(ii) A C_j that contains all the M's it intersects.

If an interval B is of type (i) we divide it into two parts: the part which is not in any C, and the C's. The first part is by definition a subset of an M_i but not of any C, and in it we therefore have $ME\varphi < \varphi$ and $CE(\varphi + \lambda\varrho^2) = \varphi + \lambda\varrho^2$, which gives

$$\begin{aligned}CE(ME\varphi + \lambda\varrho^2) &\leqq ME\varphi + \lambda\varrho^2\\&< \varphi + \lambda\varrho^2\\&= CE(\varphi + \lambda\varrho^2)\,.\end{aligned} \tag{4.13}$$

The second part is a union of sets C_j. Choosing one such C_j, we define for the given M_i,

$$\psi(\varrho) \equiv \begin{cases} ME\varphi + \lambda\varrho^2 - CE(\varphi + \lambda\varrho^2) & \text{for} \quad \varrho \in M_i - C_j\,,\\ 0 \quad \text{otherwise}\,.\end{cases} \tag{4.14}$$

Then for $\varrho \in M_i - C_j$ we have

$$\begin{aligned}CE(ME\varphi + \lambda\varrho^2) &\leqq ME\varphi + \lambda\varrho^2\\&= CE(\varphi + \lambda\varrho^2) + \psi\end{aligned} \tag{4.15}$$

and for all other ϱ, we have $\psi = 0$ and $CE(ME\varphi + \lambda\varrho^2) \leqq CE(\varphi + \lambda\varrho^2)$. This gives

$$CE(ME\varphi + \lambda\varrho^2) \leqq CE(\varphi + \lambda\varrho^2) + \psi \quad \text{for all } \varrho\,. \tag{4.16}$$

Taking the convex envelope over C'_j, the closure of C_j, of both sides of (4.16) gives

$$\begin{aligned}CE(ME\varphi + \lambda\varrho^2) &\leqq \underset{C'_j}{CE}[CE(\varphi + \lambda\varrho^2) + \psi]\\&= CE(\varphi + \lambda\varrho^2) + \underset{C'_j}{CE}\psi\end{aligned} \tag{4.17}$$

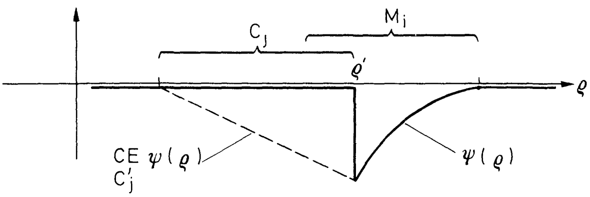

Fig. 2. Illustration of (4 · 19)

where the equality holds (see Lemma 4) because $CE(\varphi+\lambda\varrho^2)$ is linear for $\varrho\in C_j'$. But one (or possibly both) of the end points ϱ' of C_j' lies in M_i so that, from (4.14)

$$\psi(\varrho')=ME\varphi(\varrho')+\lambda\varrho'^2-\varphi(\varrho')-\lambda\varrho'^2<0\,, \tag{4.18}$$

since $ME\varphi<\varphi$ in M_i. It follows (see Fig. 2) that

$$\underset{C_j'}{CE}\psi(\varrho)<0 \quad \text{for} \quad \varrho\in C_j\,. \tag{4.19}$$

This together with (4.17) gives

$$CE(ME\varphi+\lambda\varrho^2)<CE(\varphi+\lambda\varrho^2) \quad \text{for} \quad \varrho\in C_j\,, \tag{4.20}$$

which, together with (4.13), completes the proof of (4.12) for intervals B of type (i).

Each interval B of type (ii) is a C_j and must contain at least one M_i. This is because, from Lemma 3, the function φ is convex outside the M_i's, and hence so is $\varphi+\lambda\varrho^2$. But $\varphi+\lambda\varrho^2$ cannot be convex throughout a C_j, so that no C_j can lie entirely outside the set of M_i's. Choosing any $M_i\subset C_j$, we define

$$\theta(\varrho)\equiv\begin{cases} ME\varphi+\lambda\varrho^2-CE(\varphi+\lambda\varrho^2) & \text{for} \quad \varrho=\varrho_M\,,\\ 0 \quad \text{otherwise}\,, \end{cases} \tag{4.21}$$

where ϱ_M is the point of the given M_i at which $ME\varphi=CE\varphi$ (see Lemma 2). We then have for $\varrho=\varrho_M$

$$CE(ME\varphi+\lambda\varrho^2)\leqq ME\varphi+\lambda\varrho^2=CE(\varphi+\lambda\varrho^2)+\theta\,,$$

and for $\varrho\neq\varrho_M$

$$CE(ME\varphi+\lambda\varrho^2)\leqq CE(\varphi+\lambda\varrho^2)=CE(\varphi+\lambda\varrho^2)+\theta\,,$$

so that

$$CE(ME\varphi+\lambda\varrho^2)\leqq CE(\varphi+\lambda\varrho^2)+\theta \quad \text{for all } \varrho\,. \tag{4.22}$$

Taking the convex envelope over C_j of both sides gives

$$\begin{aligned} CE(ME\varphi+\lambda\varrho^2) &\leqq \underset{C_j}{CE}[CE(\varphi+\lambda\varrho^2)+\theta]\\ &=CE(\varphi+\lambda\varrho^2)+\underset{C_j}{CE}\theta \end{aligned} \tag{4.23}$$

where the equality holds (see Lemma 4) because $CE(\varphi+\lambda\varrho^2)$ is linear for $\varrho\in C_j$. But from Lemmas 2 and 6 we have

$$ME\varphi+\lambda\varrho^2 < CE(\varphi+\lambda\varrho^2) \quad \text{for} \quad \varrho=\varrho_M, \tag{4.24}$$

and hence $\theta(\varrho_M)<0$. Since $\varrho_M\in M_i\subset C_j$, it follows (see Fig. 3) that

$$\underset{C_j}{CE}\,\theta(\varrho)<0 \quad \text{for} \quad \varrho\in C_j. \tag{4.25}$$

Together with (4.20) this gives

$$CE(ME\varphi+\lambda\varrho^2) < CE(\varphi+\lambda\varrho^2) \quad \text{for} \quad \varrho\in C_j. \tag{4.26}$$

This completes the proof of (4.12) for intervals B of type (ii), and therefore of Theorem 3.

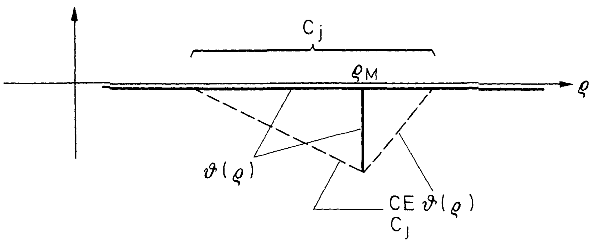

Fig. 3. Illustration of (4 · 25)

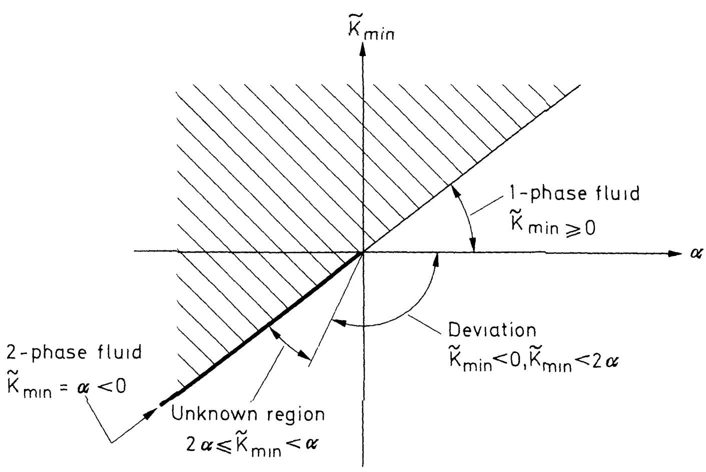

Fig. 4. Thermodynamic behaviour as determined by $\tilde{K}_{\min}$ and α. This includes the results (a) and (b) of Section I and the theorems of Section IV. Note that $\tilde{K}_{\min}\leqq\alpha$ by definition

It should be noted that for the class of Kac potentials such that $2\alpha \leqq \tilde{K}_{\min} < \alpha$ we have proved neither adherence to nor deviation from the generalized van der Waals-Maxwell theory (see Fig. 4). We cannot prove deviation because our new upper bound (2.12) coincides with that of LP (1.5) in this case. To prove this coincidence we use Lemma 5 to obtain, for $\lambda \leqq 0$ (i.e. $\tilde{K}_{\min} \geqq 2\alpha$)

$$\begin{aligned} ME\varphi &= ME(\varphi + \lambda\varrho^2 - \lambda\varrho^2) \\ &\geqq ME(\varphi + \lambda\varrho^2) + ME(-\lambda\varrho^2) \\ &= ME(\varphi + \lambda\varrho^2) - \lambda\varrho^2, \end{aligned}$$

i.e.

$$ME\varphi + \lambda\varrho^2 \geqq ME(\varphi + \lambda\varrho^2). \tag{4.27}$$

Taking the convex envelope of both sides and noting, from Lemma 1, that $CEMEf = CEf$ for any f gives, for $\lambda \leqq 0$,

$$CE(ME\varphi + \lambda\varrho^2) \geqq CE(\varphi + \lambda\varrho^2). \tag{4.28}$$

But, since $ME\varphi \leqq \varphi$, the left side of (4.28) does not exceed its right side, so that (4.28) is in fact an equality. QED.

V. The Bounds of Lebowitz and Penrose

In Section II we showed that the LP upper bound $CE(a^0 + \frac{1}{2}\alpha\varrho^2)$ on $a(\varrho, 0+)$ follows almost trivially from our variational formula (1.2). We now show that the LP lower bound, given by (1.5), which they obtained by a rather lengthy argument, also follows readily from the variational formula.

To obtain the lower bound we need

Lemma 7. *For any function $f(\varrho)$ defined on $[0, \varrho_c]$,*

$$\inf_{n \in \mathscr{C}(\varrho)} \frac{1}{|\Gamma|} \int_\Gamma d\mathbf{y}\, f[n(\mathbf{y})] = CEf(\varrho) \tag{5.1}$$

provided that the integral exists (or is infinite) for all $n \in \mathscr{C}(\varrho)$ and all $\varrho \in [0, \varrho_c]$. As before, Γ is the unit cell of n.

Proof. Denoting the left side of (5.1) by $g(\varrho)$ we have, since $\varrho \in \mathscr{C}(\varrho)$, the inequality $g(\varrho) \leqq f(\varrho)$. But, by an argument like the proof of Lemma 3 in Ref. [4], we deduce that $g(\varrho)$ is convex, and hence $g(\varrho) \leqq CEf(\varrho)$.

Now putting $h(\varrho) \equiv CEf(\varrho)$ we have, since $f(\varrho) \geqq h(\varrho)$,

$$\begin{aligned} g(\varrho) &\geqq \inf_{n \in \mathscr{C}(\varrho)} \frac{1}{|\Gamma|} \int_\Gamma d\mathbf{y}\, h[n(\mathbf{y})] \\ &\geqq \inf_{n \in \mathscr{C}(\varrho)} h\left[\frac{1}{|\Gamma|} \int_\Gamma d\mathbf{y}\, n(\mathbf{y})\right] \\ &= h(\varrho), \end{aligned} \tag{5.2}$$

where the second inequality follows [5] from the fact that $h(\varrho)$ is convex. This completes the proof of Lemma 7.

Now following LP we express K as the sum of two functions K^+ and K^- chosen so that their Fourier transforms $\tilde{K}^+$ and $\tilde{K}^-$ satisfy for all $\mathbf{p}$

$$\tilde{K}^+(\mathbf{p}) \geqq 0 \quad \text{and} \quad \tilde{K}^-(\mathbf{p}) \geqq \tilde{K}^-(0) = \tilde{K}_{\min}. \tag{5.3}$$

From (2.3), we can write $I = I^+ + I^-$, where

$$I^\pm(n) \equiv \sum_{\mathbf{p} \in V_\Gamma} \tilde{K}^\pm(\mathbf{p})\, |\tilde{n}(\mathbf{p})|^2. \tag{5.4}$$

Then from (5.3) we have

$$I^+ \geqq \tilde{K}^+(0)\, |\tilde{n}(0)|^2 = (\alpha - \tilde{K}_{\min})\varrho^2, \tag{5.5}$$

$$I^- \geqq \tilde{K}^-(0) \sum_{\mathbf{p} \in V_\Gamma} |\tilde{n}(\mathbf{p})|^2 = \tilde{K}_{\min} \frac{1}{|\Gamma|} \int_\Gamma d\mathbf{y}\, n(\mathbf{y})^2. \tag{5.6}$$

Adding these and substituting in (1.2 and 3) gives

$$a(\varrho, 0+) \geqq \inf_{n \in \mathscr{C}(\varrho)} \frac{1}{|\Gamma|} \int_\Gamma d\mathbf{y} \{a^0[n(\mathbf{y})] + \tfrac{1}{2}\tilde{K}_{\min} n(\mathbf{y})^2\} + \tfrac{1}{2}(\alpha - \tilde{K}_{\min})\varrho^2, \tag{5.7}$$

which, on application of Lemma 7, gives the desired lower bound in (1.5). We have been unable to improve on this lower bound for general functions K.

VI. Discussion

Our main results are (i) Theorem 1 which gives an upper bound (2.12) on the free energy of particle systems in the van der Waals limit, and (ii) the Theorems 2 and 3, deduced from Theorem 1, which, for the class of Kac potentials such that $\tilde{K}_{\min} < 0$ and $\tilde{K}_{\min} < 2\alpha$, give conditions under which the free energy differs from its generalized van der Waals-Maxwell form $CE[a^0 + \frac{1}{2}\alpha\varrho^2]$. For Ising magnets, the same conditions imply deviation from the Weiss theory of ferro-magnetism.

We have proved that the non-uniform periodic density (2.1) gives, in some cases, a lower value of the free energy functional $G(n)$ than does a uniform density ϱ or a two-phase mixture of uniform phases. This does not strictly prove that the minimal density is periodic since it is possible that a non-periodic function n (an almost periodic function, for example) could give a lower value of $G(n)$ than all periodic functions n. On the other hand, suppose that the infimum in (1.2) is attained for some $n^* \in \mathscr{C}(\varrho)$ (which, by the definition of $\mathscr{C}(\varrho)$, makes n^* periodic): then it follows that, in the above cases, n^* is *not* almost everywhere equal to ϱ. The system could then be described as *spatially ordered.* For Ising magnets, such ordering represents an antiferromagnetic state. It is therefore important, for the work, to find conditions under which the infimum is attained.

Conditions (c) and (d) of Section I show that the vdWM theory holds for all K if T is high or ϱ is low. The vdWM theory implies fluid states: consequently, systems with spatially ordered states have a "melting transition" in which the spatial ordering disappears. The values of $\notin$ and T for which this transition occurs, and the nature of the transition, particularly its order, have yet to be found.

As pointed out in Section II, functions n of the form (2.1) give the best upper bound when $\tilde{K}(\mathbf{p}_0) = \tilde{K}_{\min}$. This leads us to the conjecture that, if the system is one-dimensional, and $\tilde{K}(p)$ has a pronounced minimum at $p = p_0$, then the minimal function n^* (if it exists) has a period of approximately $1/p_0$. It would be interesting to determine the truth or falsity of this conjecture, and to examine, in general, the unit cell of n^*.

For the class of Kac potentials satisfying $2\alpha \leqq \tilde{K}_{\min} < \alpha$, we can prove neither adherence to nor deviation from the van der Waals-Maxwell theory. We expect that deviation occurs, but to prove this would demand a stronger upper bound than (2.12). Such a bound, if it exists, could be obtained by a better choice of n than (2.1).

It would be interesting if, in the one-dimensional case, one could find a function K in the class $\tilde{K}_{\min} < 0$, $\tilde{K}_{\min} < 2\alpha$ for which the thermodynamic functions and the density n^* could be calculated explicitly. It may be possible to perform such a calculation using the variational formula (1.2). A possible alternative approach is the method of Kac, Uhlenbeck, and Hemmer [1].

We have been able to solve many of these problems for a cell model which is closely related to the present model. For this cell model the free energy can be calculated exactly and spatial ordering can be shown to occur. We hope to present this in a future publication.

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