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Convergence of Virial Expansions*

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Some bounds are obtained on $\mathcal{R}(V)$, the radius of convergence of the density expansion for the logarithm of the grand partition function of a system of interacting particles in a finite volume V, and on $\mathcal{R}$, the radius of convergence of the corresponding infinite-volume expansion (the virial expansion). A common lower bound on $\mathcal{R}(V)$ and $\mathcal{R}$ is $0.28952/(u+1)B$, where $u \equiv \exp\,[-\mathrm{Min}\; s^{-1}\sum_{i<j\leq s} 2\varphi(\mathbf{x}_i - \mathbf{x}_j)]/\kappa T$ [so that $u \geq 1$, with equality for nonnegative $\varphi(\mathbf{r})$], $B \equiv \int |e^{-\varphi(\mathbf{r})/\kappa T} - 1|\; d^3\,\mathbf{r}$, and $\varphi(\mathbf{r})$ is the binary interaction potential; the irreducible Mayer cluster integrals have the related upper bounds $\beta_k \leq [(u+1)B/0.28952]^k/k$[$u = 1$, when $\varphi(r) \geq 0$]. For potentials with hard cores the maximum density is an upper bound on $\mathcal{R}(V)$, though possibly not on $\mathcal{R}$; an example shows how both $\mathcal{R}(V)$ and $\mathcal{R}$ can be less than the maximum density, even if there is no phase transition. A theorem is proved, analogous to Yang and Lee's theorem on uniform convergence in the complex z plane, defining a class of domains in the complex ρ plane within which the operations $V \to \infty$ and $d/d\rho$ commute. This theorem is used to show that $\lim_{V\to\infty} \mathcal{R}(V) \leq \mathcal{R}$, and that there is no phase transition for $0 \leq \rho < 0.28952/(u+1)B$.

1. INTRODUCTION

RECENTLY several authors[1-3] have obtained upper and lower bounds for the radius of convergence $R(V)$ of the Mayer fugacity expansions.[4]

$$\mathcal{V}^{-1} \log \Xi(z, V) \equiv p(z, V)/\kappa T = \sum_\ell b_\ell(V) z^\ell, \qquad (1.1)$$

$$\rho(z, V) = (z/\kappa T)\, dp(z, V)/dz = \sum_\ell \ell b_\ell(V) z^\ell. \qquad (1.2)$$

Here $\Xi(z, V)$ and $\rho(z, V)$ are the grand partition function and the mean number density at fugacity z and temperature T for a system of particles with two-body interactions, confined to a spatial region V whose volume is $\mathcal{V}$. Boltzmann's constant is denoted by κ. The coefficients $b_\ell(V)$ are the finite-volume Mayer[4] cluster integrals. The s-particle distribution functions $n_s(\mathbf{x}_1 \cdots \mathbf{x}_s \mid z, V)$ can also be expanded as power series in z, with radius of convergence at least[3] $R(V)$.

The thermodynamic pressure and density are given[1-3] for small z by

$$p(z) \equiv \lim_{V\to\infty} p(z, V) = \kappa T \sum\nolimits_\ell b_\ell z^\ell, \qquad (1.3)$$

$$\rho(z) \equiv \lim_{V\to\infty} \rho(z, V) = \sum_\ell \ell b_\ell z^\ell, \qquad (1.4)$$

where

$$b_\ell \equiv \lim_{V\to\infty} b_\ell(V) \qquad (\ell = 1, 2, \cdots). \qquad (1.5)$$

Moreover, the common radius of convergence R of these two series satisfies[3]

$$R \geq \liminf_{V\to\infty} R(V), \qquad (1.6)$$

since any point $z = a$ with $|a| < \liminf_{V\to\infty} R(V)$ must be a regular point of $p(z)$. This follows from Yang and Lee's theory.[5]

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[1] J. Groeneveld, Phys. Letters 3, 50 (1962).
[2] D. Ruelle, *Correlation Functions of Classical Gases* (Institute for Advanced Study, Princeton, 1963); Ann. Phys. (N. Y.) 25, 109 (1963).
[3] O. Penrose, J. Math. Phys. 1312 (1963).
[4] Mayer describes his theory in *Handbuch der Physik* (Springer-Verlag, Berlin, 1958), Vol. 12.
[5] C. N. Yang and T. D. Lee, Phys. Rev. 87, 404 (1952). The theory is generalized to a wider class of potentials by D. Ruelle, Helv. Phys. Acta 36, 183 (1963).

The purpose of this paper is to make a similar study of the radii of convergence $\mathcal{R}(V)$ and $\mathcal{R}$ of the finite- and infinite-volume density expansions obtained by eliminating z from (1.1) and (1.2), and from (1.3) and (1.4). These expansions may be written

$$p(z, V) = P(\rho(z, V), V) \equiv \kappa T \rho(z, V) \times \left[1 - \sum_k \frac{k}{k+1} \beta_k(V) \rho(z, V)^k\right], \quad (1.7)$$

$$p(z) = P(\rho(z)) \equiv \kappa T \rho(z) \times \left[1 - \sum_k \frac{k}{k+1} \beta_k \rho(z)^k\right]. \quad (1.8)$$

The $\beta_k(V)$'s can be expressed in terms of the $b_\ell(V)$'s by algebraic relations,[4] such as $\beta_1(V) = 2b_2(V)$, $\beta_2(V) = 3b_3(V) - 6b_2(V)^2$, etc., which do not involve V explicitly. It follows by (1.5) that

$$\beta_k = \lim_{V\to\infty} \beta_k(V). \quad (1.9)$$

The β_k's are the irreducible Mayer cluster integrals[4] and (1.8) is the virial expansion. We shall study $\mathcal{R}(V)$ by a method based on Lagrange's theorem for the expansion of one function of z in powers of another. This method incidentally yields upper bounds on the absolute values of the β_ℓ's and $\beta_\ell(V)$'s. We shall study $\mathcal{R}$ by means of a generalization to the complex ρ-plane of Yang and Lee's results[5] on uniform convergence in the z plane.

Our lower bounds on $\mathcal{R}(V)$ and $\mathcal{R}$ apply to systems of particles whose positions $\mathbf{x}_1, \mathbf{x}_2, \cdots$ are either continuously variable or confined to a lattice. Their interaction stems from a two-body interaction potential $\varphi(r)$ for which there exists a constant Φ such that

$$\sum_{i<j\le s} \varphi(\mathbf{x}_i - \mathbf{x}_j) \ge -s\Phi \quad \text{for all} \quad s, \mathbf{x}_1 \cdots \mathbf{x}_s. \quad (1.10)$$

The circumstances under which (1.10) is satisfied have been discussed by Ruelle[2,6] and Penrose.[3] We shall also make the convergence assumption

$$B \equiv \int_{\text{all space}} |e^{-\varphi(\mathbf{r})/\kappa T} - 1|\, d^\nu\mathbf{r} < \infty, \quad (1.11)$$

where ν is the number of space dimensions (= 1, 2, or 3). In discussing the upper bounds on $\mathcal{R}(V)$ and $\mathcal{R}$, we shall further assume that the potential has a hard core, i.e., that a positive constant a exists such that

$$\varphi(\mathbf{r}) = +\infty \quad \text{if} \quad r < a, \quad (1.12)$$

but this assumption is unnecessary in the other parts of the discussion.

[6] D. Ruelle, Ref. 5.

2. LAGRANGE'S THEOREM

Lagrange's theorem,[7] adapted to the expansion of $p(z, V)$ in powers of $\rho(z, V)$ may be stated thus: let the function $z/\rho(z, V)$ be analytic within and on a closed contour C surrounding the origin of the z plane, and let ρ be a complex number satisfying

$$|\rho| < \mu \equiv \operatorname*{Min}_{z \text{ on } C} |\rho(z, V)|. \quad (2.1)$$

Then the equation $\rho(z, V) = \rho$ is satisfied by just one value of z inside C, which we denote by $z(\rho, V)$; further, if the function $p(z, V)$ is analytic within and on C, it has the convergent expansion

$$P(\rho, V) \equiv p(z(\rho, V), V) = \sum_{n=1}^{\infty} c_n \rho^n, \quad (2.2)$$

where

$$c_n \equiv \frac{1}{2\pi i} \oint_{C'} \frac{dp(z, V)}{dz} \frac{dz}{n\{\rho(z, V)\}^n} = \frac{1}{n!} \frac{d^{n-1}}{dz^{n-1}} \left[\frac{dp(z, V)}{dz} \left\{\frac{z}{\rho(z, V)}\right\}^n\right]_{z=0}. \quad (2.3)$$

The path of integration is any contour C' surrounding $z = 0$ such that $|\rho(z, V)| \le \mu$ for all z on C'. The uniqueness of $z(\rho, V)$ follows from Rouché's theorem,[8] which shows that the functions z/ρ and $z/\rho - z/\rho(z, V)$ have the same number (one) of zeros inside C. The formula for c_n is obtained by expanding in powers of ρ on both sides of the following equation derived from Cauchy's residue theorem:

$$P(\rho, V) = \frac{1}{2\pi i} \oint_{C'} p(z, V) \frac{d\rho(z, V)}{dz} \frac{dz}{\rho(z, V) - \rho}, \quad (2.4)$$

and then integrating the resulting formula for c_n by parts. By virtue of the relation (1.2) between $\rho(z, V)$ and $p(z, V)$, and the definition (1.7) of the $\beta_k(V)$, Eq. (2.3) for $n = 2, 3, \cdots$ is equivalent to

$$-k\beta_k(V) = \frac{1}{2\pi i} \oint \frac{dz}{z\{\rho(z, V)\}^k} \quad (2.5)$$

for $k = 1, 2, \cdots$. This formula is used in Sec. 3 to estimate the $\beta_k(V)$'s.

3. LOWER BOUNDS ON $\mathcal{R}(V)$ AND $\mathcal{R}$

According to Lagrange's theorem, the series (2.2) converges if $|\rho|$ is less than the lower bound μ of $|\rho(z, V)|$ on the contour C; that is,

$$\mathcal{R}(V) \ge \mu \equiv \operatorname*{Min}_{z \text{ on } C} |\rho(z, V)|. \quad (3.1)$$

[7] E. T. Whittaker and G. N. Watson, *Modern Analysis* (Cambridge University Press, New York, 1927), Sec. 7.32.
[8] E. T. Copson, *Theory of Functions of a Complex Variable* (Oxford University Press, London, 1935), Sec. 6.21.

A suitable lower bound on $|\rho(z, V)|$ can be found from Penrose's generalization[3] of Groeneveld's estimates[1] of the $b_\ell(V)$'s

$$|\ell b_\ell(V)| \leq u^{\ell-2}[\ell B]^{\ell-1}/\ell! \quad (\ell = 2, 3, \cdots), \tag{3.2}$$

where

$$u \equiv e^{2\Phi/\kappa T} \geq 1, \tag{3.3}$$

and Φ and B are defined in (1.10) and (1.11). These estimates imply[1,3] that $R(V) \geq 1/euB$. In the rest of the section we ensure the convergence of (1.1) and (1.2) by requiring

$$|z| < 1/euB. \tag{3.4}$$

Since $b_1 = 1$ the series (1.1) now gives the inequality

$$\begin{aligned}|\rho(z, V) - z| &= \left|\sum_{\ell=2}^{\infty} \ell b_\ell z^\ell\right| \leq \frac{1}{u^2B}\sum_{\ell=2}^{\infty} \ell^{\ell-1}(uB\,|z|)^\ell/\ell! \\ &= w/u^2B - |z|/u,\end{aligned} \tag{3.5}$$

where w is defined by

$$we^{-w} = uB\,|z|, \qquad 0 \leq w < 1. \tag{3.6}$$

Since the function we^{-w} increases monotonically from 0 to e^{-1} in the range $0 \leq w < 1$, the condition (3.4) guarantees that w exists and is unique. In deriving the last line of (3.5) we used Euler's expansion[9] for w in powers of we^{-w}:

$$w = \sum \ell^{\ell-1}(we^{-w})^\ell/\ell!. \tag{3.7}$$

From (3.5) and (3.6) we obtain a lower bound on $|\rho(z, V)|$,

$$\begin{aligned}|\rho(z, V)| &\geq (1 + 1/u)\,|z| - w/u^2B \\ &= \{(u+1)e^{-w} - 1\}w/u^2B.\end{aligned} \tag{3.8}$$

As the contour C in (3.1), we may choose any circle $|z| = \text{const} < 1/euB$. By (3.6) the equation of this circle may be written $w = \text{const}$, and the corresponding value of μ is $\geq \{(u+1)e^{-w}-1\}w/u^2B$. Since (3.1) holds whatever value of w in the range $0 \leq w < 1$ is used to define C, we must have

$$\mathfrak{R}(V) \geq \operatorname*{Max}_{0\leq w<1} \{(u+1)e^{-w} - 1\}w/u^2B. \tag{3.9}$$

To obtain a convenient estimate of $\mathfrak{R}(V)$, we use the identity

$$\begin{aligned}\{(u+1)e^{-w} - 1\}w/u^2B \\ = \left[v - v^2 g\left(\frac{vu}{1+u}\right)\right]/(u+1)B,\end{aligned} \tag{3.10}$$

where $v \equiv w(1+u)/u$ and $g(w) \equiv (1 - e^{-w})/w$. Since $u/(1+u) \geq \frac{1}{2}$ by (3.3) and $g(w)$ decreases monotonically, the right side of (3.10) is at least $[v - v^2g(\frac{1}{2}v)]/(u+1)B$. Hence (3.9) implies

$$\begin{aligned}\mathfrak{R}(V) &\geq \operatorname*{Max}_{v}\,[v - v^2g(\tfrac{1}{2}v)]/(u+1)B \\ &= 0.28952/(u+1)B.\end{aligned} \tag{3.11}$$

The maximum is attained when $v = 0.62984$. If we had not replaced $g(vu/(1+u))$ by $g(\frac{1}{2}v)$ the numerator in (3.11) would have been replaced by a function of u increasing monotonically from 0.28952 when $u = 1$ (nonnegative potentials) to $e^{-1} = 0.36788$ as $u \to \infty$.

These methods also yield upper bounds on the $\beta_k(V)$'s. Taking the contour in (2.5) to be a circle $|z| = \text{const}$, we obtain the estimate

$$\begin{aligned}k\,|\beta_k(V)| &\leq \frac{1}{2\pi}\oint_C d\,|z| \operatorname*{Max}_{z \text{ on } C}\left|\frac{1}{z\{\rho(z, V)\}^k}\right| \\ &= [\operatorname*{Min}_{z \text{ on } C}|\rho(z, V)|]^{-k}.\end{aligned} \tag{3.12}$$

Choosing the radius of the circle, as before, to maximize the quantity in square brackets, we find that

$$\begin{aligned}k\,|\beta_k(V)| &\leq [\operatorname*{Max}_{w}\{(u+1)e^{-w} - 1\}w/u^2B]^{-k} \\ &\leq \left[\frac{(u+1)B}{0.28952}\right]^k \qquad (k = 1, 2, \cdots).\end{aligned} \tag{3.13}$$

Combined with (1.5) this gives upper bounds on the irreducible Mayer cluster integrals

$$k\,|\beta_k| \leq [(u+1)B/(0.28952)]^k. \tag{3.14}$$

This set of inequalities implies, by (1.8) and Cauchy's kth-root convergence test, that

$$\begin{aligned}\mathfrak{R} &= \liminf_{k\to\infty}\left|\frac{k}{k+1}\beta_k\right|^{-1/k} \\ &\geq 0.28952/(u+1)B,\end{aligned} \tag{3.15}$$

so that $\mathfrak{R}$ and $\mathfrak{R}(V)$ have the same lower bound. The result (3.15) can also be obtained by applying to the function $\rho(z)$ the same arguments which when applied to $\rho(z, V)$ led to (3.11); or by using (6.1).

4. UPPER BOUND ON $\mathfrak{R}(V)$

One way of finding an upper bound on $\mathfrak{R}(V)$ is to locate singularities of the analytic continuation of the function $P(\rho, V)$ defined for small ρ in Sec. 2. This analytic continuation is easiest for the physically possible values of ρ.

The physically possible values of z are the real

[9] G. Pólya and G. Szegö, *Aufgaben und Lehrsätze der Analysis* (Springer-Verlag, Berlin, 1925), Vol. I, Part III, Chap. 5, No. 209.

positive values. The theory of fluctuations shows that $d\rho(z, V)/dz = [\langle N^2\rangle - \langle N\rangle^2]/z\mathcal{V}$ is positive for positive z. Therefore, as z increases from 0 to ∞, $\rho(z, V)$ increases monotonically from 0 to some limiting value $\rho_M(V)$, (which may be $+\infty$) and $p(z, V) = \kappa T \int_0^z \rho(z, V)\, dz/z$ increases monotonically from 0 to ∞. Thus the physically possible values of ρ are $0 < \rho < \rho_M(V)$. For hard-core potentials $\rho_M(V)$ is given by

$$\rho_M(V) = M(V)/\mathcal{V}, \tag{4.1}$$

where $M(V)$ is the largest number of nonintersecting spheres of diameter a whose centers can be fitted into the region V. For potentials without hard cores, $\rho_M(V)$ is $+\infty$.

Since $\rho(z, V)$ increases monotonically for $0<z<\infty$, its inverse function $z(\rho, V)$—although many-valued—has a branch $Z(\rho, V)$, which increases monotonically from 0 to ∞ as ρ increases from 0 to $\rho_M(V)$. For the physically possible values of ρ we may therefore define $P(\rho, V)$ by

$$P(\rho, V) \equiv p(Z(\rho, V), V) \quad (0 < \rho < \rho_M). \tag{4.2}$$

This function increases monotonically from 0 to ∞, and is therefore singular at $\rho = \rho_M(V)$. Moreover, the two definitions (2.2) and (4.2) are equivalent when $0 < \rho < 0.28952/(u + 1)B$. It follows that the series (2.2) must diverge when $\rho = \rho_M(V)$, so that

$$\mathcal{R}(V) \leq \rho_M(V). \tag{4.3}$$

Unfortunately this upper bound provides information only for hard-core potentials.

Taking the limit $V \to \infty$ we obtain[10]

$$\lim_{V\to\infty} \mathcal{R}(V) \leq \rho_M \equiv \lim_{V\to\infty} \rho_M(V). \tag{4.4}$$

To obtain an upper bound on $\mathcal{R}$ we may try using the same argument for $\rho(z)$ and $z(\rho)$ instead of $\rho(z, V)$ and $z(\rho, V)$. Provided that the system has no phase transition [so that $\rho(z)$ is analytic at every point on the positive z axis], and provided that

$$d\rho(z)/dz > 0 \quad \text{for all} \quad z > 0, \tag{4.5}$$

the same argument goes through, giving

$$\mathcal{R} \leq \rho_M \equiv \lim_{V\to\infty} \rho_M(V) \tag{4.6}$$

if there is no phase transition. However, if there is a phase transition, $\mathcal{R}$ may perhaps be larger than ρ_M. The approximate equation of state found by Reiss, Frisch, and Lebowitz[11] for the hard-sphere fluid illustrates this possibility since its only singularity is a triple pole at $\rho = 6\rho_M/\pi\sqrt{2} = 1.3505\rho_M$ which suggests that $\mathcal{R} \cong 1.3505\rho_M > \rho_M$.

[10] If the limits in (4.4) do not exist, the inequality is true for both the largest and the smallest limit points of $\mathcal{R}(V)$ and $\rho_M(V)$.

5. YANG–LEE THEORY FOR THE ρ PLANE

In this section we generalize Yang and Lee's theory of uniform convergence in the z plane by proving a corresponding theorem for the ρ plane. This theorem indicates, for example, the circumstances under which the operations $\lim_{V\to\infty}$ and $d/d\rho$ are interchangeable.

Theorem. Let $\rho_1 < \rho < \rho_2$ be a segment of the real ρ axis, with $0 \leq \rho_1$ and $\rho_2 < \rho_M$. Let $\mathfrak{D}$ be any bounded simply connected region in the ρ plane, whose intersection with the line segment $0 < \rho < \rho_M$ is the set $\rho_1 < \rho < \rho_2$, and into which analytic continuation of the functions $P(\rho, V)$ defined by (4.2) yields a single-valued regular function for all sufficiently large V. Then the sequence of functions $P(\rho, V)$ converges uniformly on any region bounded by a contour inside $\mathfrak{D}$.

Proof: The proof depends on Vitali's theorem[12] which states that, if $\mathfrak{D}$ is a region and $f(\rho, V)$ is a sequence of analytic functions which are

(i) regular in $\mathfrak{D}$,
(ii) uniformly bounded in $\mathfrak{D}$,
(iii) convergent, as $V \to \infty$, on a set of points having a limit point in $\mathfrak{D}$,

then the sequence $f(\rho, V)$ converges uniformly in any region bounded by a contour inside $\mathfrak{D}$. We shall apply Vitali's theorem to the sequence

$$f(\rho, V) \equiv \rho/Z(\rho, V), \tag{5.1}$$

where $Z(\rho, V)$ is the analytic continuation, into $\mathfrak{D}$, of the function $Z(\rho, V)$ defined for $0 < \rho < \rho_M$ in Sec. 4. We start the sequence (5.1) with V sufficiently large to make the analytic continuation of $P(\rho, V)$ into $\mathfrak{D}$ possible for all larger V. According to the definitions (1.1) and (1.7), the functions $f(\rho, V)$ and $P(\rho, V)$ are related by the differential equation

$$\frac{1}{\kappa T}\frac{dP(\rho, V)}{d\rho} = 1 - \rho\frac{d[\log f(\rho, V)]}{d\rho}. \tag{5.2}$$

[11] H. Reiss, H. L. Frisch and J. L. Lebowitz [J. Chem. Phys. 31, 369 (1959)] find that $\rho/\rho\kappa T \simeq (1 + \alpha + \alpha^2)/(1 - \alpha)^3$ where $\alpha = \sqrt{2}\pi\rho/6\rho_M$. The same equation of state also follows from the Percus–Yevick equation: see M. Wertheim, Phys. Rev. Letters 8, 321 (1963); E. Thiele, J. Chem. Phys. 39, 474 (1963).

[12] E. C. Titchmarsh, *The Theory of Functions* (Oxford University Press, London, 1939), 2nd ed., p. 168.

Since $P(\rho, V)$ is regular and $\mathfrak{D}$ is simply connected, it follows that $\log f(\rho, V)$ is regular and single-valued in $\mathfrak{D}$; therefore, the analytic continuation used in the definition (5.1) leads to no ambiguities, and moreover $f(\rho, V)$ satisfies the condition (i) of Vilati's theorem.

To deal with the condition (ii), consider first the part of $\mathfrak{D}$ where $Z(\rho, V) \geq 1/euB$. Clearly $f(\rho, V)$ is bounded in this part, since the denominator of (5.1) is bounded away from zero and the numerator is bounded because $\mathfrak{D}$ is a bounded region of the ρ plane. For the other part of $\mathfrak{D}$, where $Z(\rho, V) < 1/euB$, we write z for $Z(\rho, V)$ and use (3.5) to show that

$$|\rho(z, V)| \leq w/u^2B + (1 - 1/u)\,|z| \leq w/uB, \tag{5.3}$$

so that

$$|f(\rho, V)| = \left|\frac{\rho(z, V)}{z}\right| \leq w/|z|\,uB = e^{w} \leq e. \tag{5.4}$$

Thus $f(\rho, V)$ is bounded in both parts of $\mathfrak{D}$, and (ii) is satisfied.

To show that the sequence defined in (5.1) satisfies condition (iii) it is sufficient to show that, as $V \to \infty$, $Z(\rho, V)$ converges to a limit at almost all points on the segment $\rho_1 < \rho < \rho_2$, since then any subsegment $\rho_1' \leq \rho < \rho_2'$, where $\rho_1 < \rho_1' < \rho_2' < \rho_2$, lies within $\mathfrak{D}$ and contains[13] at least one limit point of the points where $Z(\rho, V)$ converges.

We shall begin by proving the corresponding convergence property for the function $\rho(z, V)$ of which $Z(\rho, V)$ is the inverse. The proof depends on the fact, proved in Sec. 4, that $\rho(z, V)$ is an increasing function of z for real positive z; this fact implies that, for any positive z,

$$\rho(z, -h, V) \leq \rho(z, V) \leq \rho(z, h, V), \tag{5.5}$$

where h is a positive number less than z, and

$$\rho(z, \pm h, V) \equiv h^{-1}\int_0^h \rho(z \pm t, V)\, dt/t \tag{5.6}$$

$$= [p(z \pm h, V) - p(z, V)]/(\pm h\kappa T) \tag{5.7}$$

by (1.2). It is known from Yang and Lee's theory[5] that

$$p(z) \equiv \lim_{V\to\infty} p(z, V) \tag{5.8}$$

exists for all positive z; therefore taking the limit $V \to \infty$ in (5.5) gives

$$\rho(z, -h) \leq \liminf_{V\to\infty} \rho(z, V) \leq \limsup_{V\to\infty} (\rho(z, V) \leq \rho(z, +h)), \tag{5.9}$$

[13] Ref. 7, Sec. 2.21, p. 12.

where

$$\rho(z, \pm h) \equiv [p(z \pm h) - p(z)]/(\pm h\kappa T). \tag{5.10}$$

Taking the limit $h \to 0$ in (5.9) we find that $\lim_{V\to\infty} \rho(z, V)$ exists, and is equal to $(z/\kappa T)\, dp(z)/dz$, for all positive values of z where $dp(z)/dz$ exists. But $p(z)$, being a nondecreasing function, is[14] differentiable for almost all z; therefore

$$\rho(z) \equiv \lim_{V\to\infty} \rho(z, V) \tag{5.11}$$

exists for almost all positive values of z.

Since the $\rho(z, V)$'s are increasing functions, the limit function $\rho(z)$ is nondecreasing. Its inverse function $z(\rho)$ is therefore uniquely defined[15] for all values of ρ satisfying $0 < \rho < \rho_M$, apart from a set of exceptional values of ρ for which the equation $\rho = \rho(z)$ has more than one solution. Each exceptional value corresponds to a segment of the real z axis on which $\rho(z)$ is constant. Since these segments of the z axis are countable, the exceptional values of ρ form a set of zero measure.

To show that $\lim Z(\rho, V)$ exists, let ρ_0 be any nonexceptional value of ρ, let $z_0 \equiv Z(\rho_0)$, and let ϵ be a small positive number such that $\rho(z_0 - \epsilon)$ and $\rho(z_0 + \epsilon)$ exist. Since $\rho(z)$ is monotonic and ρ_0 is nonexceptional, we have $\rho(z_0 - \epsilon) < \rho_0 < \rho(z_0 + \epsilon)$, and hence by (5.11) the inequality

$$\rho(z_0 - \epsilon, V) < \rho_0 < \rho(z_0 + \epsilon, V) \tag{5.12}$$

holds for all sufficiently large V. Applying the nondecreasing function $Z(\rho, V)$ to (5.12) we find

$$z_0 - \epsilon \leq Z(\rho_0, V) \leq z_0 + \epsilon. \tag{5.13}$$

Since ϵ can be made arbitrarily small, it follows that

$$\lim_{V\to\infty} Z(\rho_0, V) = z_0 = Z(\rho_0) \tag{5.14}$$

for almost all values of ρ_0 in the range $0 < \rho < \rho_M$. Consequently, condition (iii) of Vitali's theorem is satisfied.

Vitali's theorem now tells us that the sequence $f(\rho, V)$ converges uniformly in any region bounded by a contour inside $\mathfrak{D}$; its limiting function $f(\rho)$ is therefore regular inside $\mathfrak{D}$. To prove our theorem that the same is true of the sequence $P(\rho, V)$ we consider two cases separately. Suppose first that $f(\rho)$ has a zero inside $\mathfrak{D}$, say at $\rho = \alpha$. The value of α cannot be zero, since if the point $\rho = 0$ is within $\mathfrak{D}$ then the conditions of the theorem imply

[14] Ref. 12, Sec. 11.42.

[15] Either as the solution of $\rho = \rho(z)$ or, if this has no solution, by means of a Dedekind section of the real z axis.

that the segment of the nonnegative real axis inside $\mathfrak{D}$ is $0 \leq \rho < \rho_2$, so that by continuity $f(0) = \lim_{\rho\to 0+} \rho/Z(\rho, V) = \lim_{z\to 0} \rho(z, V)/z = 1 \neq 0$. By Hurwitz's theorem,[16] all the $f(\rho, V)$'s for large enough V must also have zeros at points near $\rho = \alpha \neq 0$ inside $\mathfrak{D}$. Hence, by (5.2), all the $P(\rho, V)$'s for large enough V have logarithmic singularities at these points. This contradicts the condition that the $P(\rho, V)$'s must be single-valued within $\mathfrak{D}$ for large enough V, and thus rules out this first case where $f(\rho)$ has a zero inside $\mathfrak{D}$.

In the remaining case the function $f(\rho)$, having no zeros inside $\mathfrak{D}$, must be bounded away from zero inside any contour within $\mathfrak{D}$; consequently all the $f(\rho, V)$'s are also bounded away from zero inside the contour for large enough V. It follows that the sequence $\log f(\rho, V)$ converges uniformly within the contour, and so also do[17] the sequences $d(\log f(\rho, V))/d\rho$ and [by (5.2)] $dP(\rho, V)/d\rho$. Evaluating $P(\rho, V)$ by integration of its derivative along a path inside $\mathfrak{D}$ with one end fixed on the positive real axis, we conclude[17] that the sequence $P(\rho,V)$ does converge uniformly within the contour. Q.E.D.

6. RELATION BETWEEN $\mathfrak{R}$ AND lim $\mathfrak{R}(V)$

The theorem of Sec. 5 leads at once to a result analogous to (1.6). Let δ be any small positive number. Then the disk $|\rho| < \liminf_{V\to\infty} \mathfrak{R}(V) - \delta$ satisfies the conditions required of the region $\mathfrak{D}$, since the power series (2.2) whose radius of convergence exceeds the radius of $\mathfrak{D}$ for all sufficiently large V, provides the analytic continuation of $P(\rho, V)$ from the real axis into $\mathfrak{D}$. The theorem then implies that $P(\rho)$, being the limit of a uniformly convergent sequence of analytic functions, is itself analytic inside the contour $|\rho| = \liminf_{V\to\infty} \mathfrak{R}(V) - 2\delta$. Therefore the power-series expansion (1.8) for $P(\rho)$ converges if $|\rho| \leq \liminf_{V\to\infty} \mathfrak{R}(V) - 2\delta$. Since δ can be made arbitrarily small, it follows that

$$\liminf_{V\to\infty} \mathfrak{R}(V) \leq \mathfrak{R}. \qquad (6.1)$$

7. OTHER DENSITY EXPANSIONS

Besides the pressure, other quantities have useful expansions in powers of ρ. We can relate their radii of convergence to $\mathfrak{R}$ and $\mathfrak{R}(V)$.

Foremost among these expansions is that of the fugacity z. Since the analytic functions $P(\rho, V)$ and $Z(\rho, V)$ are both regular near $\rho = 0$, it follows from the differential equation (5.2) that their singularities in the ρ plane (appropriately cut) coincide, and hence that the series expansion of $Z(\rho, V)$ has radius of convergence $\mathfrak{R}(V)$. Similarly, the series expansion of $Z(\rho) \equiv \lim_{V\to\infty} Z(\rho, V)$ has radius of convergence $\mathfrak{R}$.

The density expansions for the s-particle distribution functions $n_s(\mathbf{x}_1, \cdots \mathbf{x}_s)$ are also important. To study their convergence, consider the disk $|\rho| < \mathfrak{R}(V)$ and its image D in the z plane under the mapping $z = Z(\rho, V)$. Since the function $\rho(z, V)$ is single-valued, it is regular within D; therefore[5] $\Xi(z, V)$ has no zeros in D, so that[3] $n_s(\mathbf{x}_1, \cdots \mathbf{x}_s)$ is a regular function of z within D. It follows that $n_s(\mathbf{x}_1, \cdots \mathbf{x}_s)$ is a regular function of ρ within $|\rho| < \mathfrak{R}(V)$, so that its expansion in powers of ρ has radius of convergence at least $\mathfrak{R}(V)$.

8. DISCUSSION

The information we have obtained about $\mathfrak{R}(V)$ and $\mathfrak{R}$ can be summarized in the formulas

$$0.28952/(u + 1)B \leq \mathfrak{R}(V) \leq \rho_M(V), \qquad (8.1)$$

$$\liminf_{V\to\infty} \mathfrak{R}(V) \leq \mathfrak{R}, \qquad (8.2)$$

which come from (3.11), (4.3), and (6.1). The quantities u, B, and $\rho_M(V)$ are defined in (3.3), (1.11), and (4.1).

The simplest illustration of these formulas is provided by a system of hard rods in one dimension. Its equation of state is

$$P/\kappa T = \rho/(1 - a\rho) = \rho + a\rho^2 + \cdots, \qquad (8.3)$$

where a is the length of each rod. The value of $\mathfrak{R}$ is therefore $1/a$. The value of $\liminf_{V\to\infty} \mathfrak{R}(V)$ is harder to calculate, but (8.1) and (8.2) provide the rather wide bounds

$$0.07238 \leq a \liminf_{V\to\infty} \mathfrak{R}(V) \leq 1 \qquad (8.4)$$

since $u = 1$, $B = 2a$, and $\rho_M = 1/a$.

The main physical conclusion to be drawn from our results is that there can be no phase transition for densities less[18] than $0.28952/(u + 1)B$, since the series (1.7) converges for these densities and is equal (by the theorem of Sec. 5) to the thermodynamic pressure, which is therefore an analytic

[16] Ref. 12, Sec. 3.45.

[17] Ref. 8, Secs. 5.13 and 5.12.

[18] D. Ruelle, Ref. 2, shows that for nonnegative potentials there can be no phase transition for densities less than $1/3.8B = 0.26/B$. Using an inequality due to E. Lieb [J. Math. Phys. 4, 671 (1963)], this number can be slightly increased to $1/(1 + e)B = 0.27/B$. For general hard-core potentials the corresponding number is $1/u[(1 + e)B_+ + eB_-]$, where B_+ and B_- are the contributions of the positive and negative parts of $\varphi(r)$ to the integral (1.1) [see O. Penrose, J. Math. Phys. 4, 1488 (1963), Eq. (8.3)]. For more general potentials, however, the bound $0.28952/(u + 1)B$ given in the text is the best available.

function of ρ. Moreover, if lim inf $\mathcal{R}(V)$ is known, it provides a better lower bound on the density at a phase transition. This follows from the arguments of Secs. 5 and 6.

On the other hand, our results do not prove that $\mathcal{R}$ is a lower bound on the density at a phase transition. For quantum systems, Fuchs[19] has shown that $\mathcal{R}$ can actually exceed the value of ρ at a phase transition (for an ideal B–E gas). For classical systems the question remains open, although the example mentioned at the end of Sec. 4 suggests that here too, $\mathcal{R}$ can exceed the value of ρ at a phase transition.[20]

Although the value of ρ at the first phase transition cannot be less than lim inf $\mathcal{R}(V)$, it can be greater than both lim inf $\mathcal{R}(V)$ and $\mathcal{R}$. This can be shown by considering a one-dimensional system of interacting hard rods with the interaction potential

$$\varphi(r) = \begin{cases} +\infty & (|r| < a), \\ \kappa T \ln 2 & (a \leq |r| < 2a), \\ 0 & (2a \leq |r|). \end{cases} \tag{8.5}$$

For this potential, fugacity and pressure are related by[21]

$$\frac{1}{Z} = \int_0^\infty e^{-[rp+\varphi(r)]/\kappa T}\, dr$$

$$= \frac{\kappa T}{p} e^{-3ap/2\kappa T} \cosh(ap/2\kappa T), \tag{8.6}$$

so that

$$\frac{1}{\rho\kappa T} = \frac{d(\ln z)}{dp} = \frac{1}{p} + \frac{3a}{2\kappa T} - \frac{a}{2\kappa T}\tanh\frac{ap}{2\kappa T}. \tag{8.7}$$

As p moves in its Argand plane from the origin along the positive imaginary axis, the value of $1/\rho - \frac{3}{2}a$ moves along its imaginary axis from $-i\infty$ to a value $-(1.1322)ia$, achieved when $p = 2ix\kappa T/a$ where $x = 0.7393$ is the real solution of $x = \cos x$, and then retreats again to $-i\infty$. Hence the image point of ρ starts at the origin of its Argand plane, moves along a circular arc whose furthest point from the origin is its other end at $1/(1.5000 - 1.1322i)a$, and returns to the origin. Therefore the function $P(\rho)$ has a branch point at $1/(1.5000 - 1.1322i)a$, and $\mathcal{R}$ is at most $1/|1.5000 - 1.1322i|\, a = \frac{1}{2}(0.5321)$, which is less than $\rho_M = 1/a$. Thus, for this system, unlike the simple hard-rod system, both $\mathcal{R}$ and lim inf $\mathcal{R}(V)$ are less than ρ_M, despite the fact that there is no phase transition for $0 < \rho < \rho_M$. Therefore, the actual values of $\mathcal{R}$ and $\liminf_{V\to\infty} \mathcal{R}(V)$ have, in general, no physical significance since they may be determined by singularities off the real positive ρ axis.[22]

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[19] W. H. J. Fuchs, J. Ratl. Mech. Anal. 4, 647 (1955).

[20] M. Kac, G. E. Uhlenbeck and P. C. Hemmer, J. Math. Phys. 4, 216 (1963), consider a one-dimensional system with

$$\varphi(r) = \begin{cases} \infty & |r| < a \\ -2\alpha\gamma e^{-\gamma r}, & |r| > a, \end{cases}$$

and find that this system has a phase transition in the limit $\gamma \to 0$, which can be obtained from Maxwell's equal area construction applied to

$$p_0(\rho) = \kappa T\left[\frac{\rho}{1-\rho a} - \alpha\rho^2\right] = \kappa T\rho\left[1 - \sum_k \frac{k}{k+1}\beta_k{}^0\rho^k\right],$$

where $\beta_k{}^0 = \lim_{\gamma\to 0}\beta_k(\gamma)$, and $\beta_k(\gamma) = \lim_{V\to\infty}\beta_k(\gamma, V)$. Thus $\mathcal{R}^0 = a^{-1}$, the radius of convergence of the above series exceeds the value of ρ at the phase transition.

[21] H. Takahasi, Proc. Phys. Soc. Japan 24, 60 (1942); F. Gursey, Proc. Cambridge Phil. Soc. 46, 182 (1950).

[22] The nearest singularity of $P(\rho)$ is off the real positive ρ axis if and only if an infinite number of virial coefficients are negative. This example therefore supplements Wertheim's proof that the virial coefficients need not all be positive even if $\varphi(r)$ is nonnegative. [Wertheim considers the case $\varphi(r) \propto r^{-n}$; forthcoming paper.]