

New Series Expansion in Statistical Mechanics*

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A new approximation scheme is applied to thermodynamic variables which have power-series expansions in terms of real parameters. This method is based upon a previously discussed formula designed to overcome the convergence difficulties of the quantum-mechanical Born (perturbation) series. Some properties of the approximation scheme are obtained, and then the method is used to obtain information from power-series expansions such as those met with in thermodynamics and statistical mechanics. In particular, the virial coefficients for several molecular models are used to obtain numerical approximations to the equations of state. The solution for a one-dimensional system of hard rods is obtained exactly in this scheme. For the two-dimensional hard-square lattice gas, the results agree quite well with recent low- and high-density Padé approximants. The qualitative behavior of the solution for a system of hard spheres resembles that of the Mayer theory of condensation. It is noteworthy that the approximation scheme has the property of generating solutions which are monotonically increasing in the density. Thus, no van der Waals loop is obtained.

I. INTRODUCTION

PHYSICALLY interesting effects cannot always be treated by series expansions. In some instances, the maximum information which can be obtained from such expansions is not well understood. However, the necessity for series expansion is well known in many different areas of research. Therefore, it is worthwhile to obtain an approximation scheme which replaces the series by a more convergent expansion which may give substantial results and a better understanding of the problem under consideration.

In the present work, we use a formula¹ designed to overcome the convergence difficulties of the Born series for a quantum-mechanical system. We shall limit ourselves to the virial expansions of imperfect gases and to the virial expansions of a two-dimensional lattice gas (Ising model) with the inclusion of attractive as well as repulsive forces. The goal, however, is to introduce the method into the theory of statistical mechanics where it may be of great value and applicability.

This method can be used easily for the study of many other thermodynamic variables. Further, it can be extended to the study of systems of several expansion parameters.² Hence, it is of wide generality as attested also by its use in field theory. For example, the method has been applied recently to a field-theoretical model for pion-pion scattering giving results³ quite consistent with experiment.

This new approximation scheme has little resemblance to any other method in use in statistical mechanics. The lowest order approximation resembles the so-called [1,1] Padé approximant⁴; however, this

similarity is only delusive and does not persist to higher order.

II. FORMAL DERIVATION

The basic equation is developed in this section. The derivation is somewhat different from the one originally given in Ref. 1 to improve the Born series; however, at each stage a similarity is apparent.

Let $\eta(t; g)$ be some thermodynamic variable as the pressure P or the magnetic susceptibility χ , etc., where t is some continuous variable and g is a real adjustable parameter. Suppose $\eta(t; g)$ possesses the series expansion

$$\eta(t; g) = \eta_0(t) + \eta_1(t)g + \eta_2(t)g^2 + \dots, \quad (2.1)$$

where $\eta_j(t)$ ($j=1, 2, \dots$) are differentiable and $\eta_1(t) \neq 0$ on an interval I of t . The series (2.1) need not be a convergent series. What is of interest is the sequence $\{\eta_n(t)\}$ generated by the expansion. We consider the formation of the inverse power series of (2.1). There exists precisely one power series formally satisfying this condition, and this is

$$g = \frac{\eta - \eta_0}{\eta_1} - \frac{\eta_2(\eta - \eta_0)^2}{\eta_1^2} + \left[2 \left(\frac{\eta_2}{\eta_1} \right)^2 - \frac{\eta_3}{\eta_1} \right] \left(\frac{\eta - \eta_0}{\eta_1} \right)^3 + \left[5 \frac{\eta_2 \eta_3}{\eta_1^2} - \frac{\eta_4}{\eta_1} - 5 \left(\frac{\eta_2}{\eta_1} \right)^3 \right] \left(\frac{\eta - \eta_0}{\eta_1} \right)^4 + \dots, \quad (2.2)$$

where the explicit dependence of the function on t has been omitted for conciseness.

The formal inversion of the real parameter g can be accomplished only in regions of the variable t where the complex phases of the functions $\eta_1(t)$, $\eta_2(t)$, \dots are all the same. These are the so-called constant-phase regions introduced in Ref. 1. We suppose the interval I is one such region.

It is clear that the left-hand side of (2.2) is independent of t . Hence, by evaluating the right-hand side of (2.2) for $t = \tau$, say, and substituting the resulting

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¹ M. Wellner, Phys. Rev. **132**, 1848 (1963).

² M. Alexanian (to be published).

³ M. Alexanian and M. Wellner, Phys. Rev. **137**, B155 (1965).
M. Alexanian and M. Wellner, *ibid.*, Phys. Rev. **140**, B1079 (1965).

⁴ G. A. Baker, Jr., J. L. Gammel, and J. G. Wills, J. Math. Anal. Appl. **2**, 405 (1961).

form into (2.1) yields

$$\tilde{\eta}(t) = \tilde{\eta}(\tau) + \left[\frac{\eta_2(t)}{\eta_1(t)} - \frac{\eta_2(\tau)}{\eta_1(\tau)} \right] \tilde{\eta}^2(\tau) + \left[\frac{\eta_3(t)}{\eta_1(t)} - \frac{\eta_3(\tau)}{\eta_1(\tau)} - 2 \frac{\eta_2(\tau)}{\eta_1(\tau)} \frac{\eta_2(t)}{\eta_1(t)} + 2 \frac{\eta_2^2(\tau)}{\eta_1^2(\tau)} \right] \tilde{\eta}^3(\tau) + \dots, \quad (2.3)$$

where

$$\tilde{\eta}(t) \equiv \frac{\eta(t) - \eta_0(t)}{\eta_1(t)}.$$

This is the same as Eq. (3.9) of Ref. 1 and contains the statement of fast convergence enforced in the interval I at $t = \tau$.

The basic differential equation is obtained by taking the derivative of (2.1) with respect to t , which yields

$$\tilde{\eta}' = \left(\frac{\eta_2}{\eta_1} \right)' g^2 + \left(\frac{\eta_3}{\eta_1} \right)' g^3 + \dots \left(' = \frac{d}{dt} \right), \quad (2.4)$$

and then by substituting g from (2.2) into (2.4) which yields

$$\begin{aligned} \tilde{\eta}' = & \left(\frac{\eta_2}{\eta_1} \right)' \tilde{\eta}^2 + \left[2g_1 \left(\frac{\eta_2}{\eta_1} \right)' + \left(\frac{\eta_3}{\eta_1} \right)' \right] \tilde{\eta}^3 + \left[(g_1^2 + 2g_2) \left(\frac{\eta_2}{\eta_1} \right)' + 3g_1 \left(\frac{\eta_3}{\eta_1} \right)' + \left(\frac{\eta_4}{\eta_1} \right)' \right] \tilde{\eta}^4 \\ & + \left[(2g_1g_2 + 2g_3) \left(\frac{\eta_2}{\eta_1} \right)' + (3g_1^2 + 3g_2) \left(\frac{\eta_3}{\eta_1} \right)' + 4g_1 \left(\frac{\eta_4}{\eta_1} \right)' + \left(\frac{\eta_5}{\eta_1} \right)' \right] \tilde{\eta}^5 \\ & + \left[(g_2^2 + 2g_4 + 2g_1g_3) \left(\frac{\eta_2}{\eta_1} \right)' + (g_1^3 + 3g_3 + 6g_1g_2) \left(\frac{\eta_3}{\eta_1} \right)' + (6g_1^2 + 4g_2) \left(\frac{\eta_4}{\eta_1} \right)' + 5g_1 \left(\frac{\eta_5}{\eta_1} \right)' + \left(\frac{\eta_6}{\eta_1} \right)' \right] \tilde{\eta}^6 \\ & + \left[(2g_5 + 2g_1g_4 + 2g_2g_3) \left(\frac{\eta_2}{\eta_1} \right)' + (3g_4 + 6g_1g_3 + 3g_1^2g_2 + 3g_2^2) \left(\frac{\eta_3}{\eta_1} \right)' + (4g_1^3 + 12g_1g_2 + 4g_3) \left(\frac{\eta_4}{\eta_1} \right)' \right. \\ & \left. + (10g_1^2 + 5g_2) \left(\frac{\eta_5}{\eta_1} \right)' + 6g_1 \left(\frac{\eta_6}{\eta_1} \right)' + \left(\frac{\eta_7}{\eta_1} \right)' \right] \tilde{\eta}^7 + \dots, \quad (2.5) \end{aligned}$$

where

$$\begin{aligned} g_1 = & -\frac{\eta_2}{\eta_1}, \\ g_2 = & -\frac{\eta_3}{\eta_1} + 2 \left(\frac{\eta_2}{\eta_1} \right)^2, \\ g_3 = & -\frac{\eta_4}{\eta_1} + 5 \frac{\eta_3}{\eta_1} \frac{\eta_2}{\eta_1} - 5 \left(\frac{\eta_2}{\eta_1} \right)^3, \\ g_4 = & -\frac{\eta_5}{\eta_1} + 6 \frac{\eta_2}{\eta_1} \frac{\eta_4}{\eta_1} + 3 \left(\frac{\eta_3}{\eta_1} \right)^2 - 21 \left(\frac{\eta_2}{\eta_1} \right)^2 \frac{\eta_3}{\eta_1} + 14 \left(\frac{\eta_2}{\eta_1} \right)^4, \\ g_5 = & -\frac{\eta_6}{\eta_1} + 7 \frac{\eta_2}{\eta_1} \frac{\eta_5}{\eta_1} - 28 \left(\frac{\eta_2}{\eta_1} \right)^2 \frac{\eta_4}{\eta_1} + 7 \frac{\eta_3}{\eta_1} \frac{\eta_4}{\eta_1} \\ & + 84 \frac{\eta_3}{\eta_1} \left(\frac{\eta_2}{\eta_1} \right)^3 - 28 \left(\frac{\eta_3}{\eta_1} \right)^2 \frac{\eta_2}{\eta_1} - 42 \left(\frac{\eta_2}{\eta_1} \right)^5. \quad (2.6) \end{aligned}$$

Since the real parameter g has been eliminated between the two equations (2.2) and (2.4), it must be related to the constant of integration K of the first-order differential equation (2.5). This dependence on g signifies the replacement of one parameter in terms of another. The constant of integration $K(g)$ is determined

by a knowledge of the *exact* value of $\eta(t; g)$ at some point $t = t_0$.

If instead of the real parameter g , the parameter $\hat{g} = g/g_0$ is introduced in the expansion (2.1), where g_0 is real and independent of t , the same differential equation (2.5) is obtained for $\tilde{\eta}$. In general, if η is the function associated with the sequence $\{\eta_n(t)\}$ and η^* with the sequence $\{\eta_n(t)h^n\}$, where h is nonzero and independent of t , then $\eta = \eta^*$. Herein lies the connection of this method to the renormalization-group method of field theory.²

III. EXISTENCE AND UNIQUENESS OF THE IMPROVED SOLUTION

In the preceding section, a first-order nonlinear differential equation was obtained for the function $\eta(t)$ which is of the form

$$\frac{d\tilde{\eta}}{dt} = \sum_{k=2}^{\infty} a_k(t) [\tilde{\eta}(t)]^k \equiv f(\tilde{\eta}, t), \quad (3.1)$$

where the function $a_k(t)$ depends on the coefficients $\eta_1(t), \eta_2(t), \dots, \eta_k(t)$. The right-hand side of (3.1) was derived formally by inverting a power series and is presumed to optimize the convergence of $\tilde{\eta}(t)$ in the region of constant phase,

We now consider the solutions of (3.1) which presuppose a knowledge only of a finite number of coefficients of (2.1). Suppose $n+1$ such coefficients are known, $\eta_0(t)$, $\eta_1(t)$, \dots , $\eta_n(t)$. The solution is called the n th order improved solution (because of the forced convergence) and satisfies the equation

$$\frac{d\tilde{\eta}_n}{dt} = \sum_{k=2}^n a_k(t) [\tilde{\eta}_n(t)]^k \equiv f_n(\tilde{\eta}_n, t), \quad (3.2)$$

where

$$\eta_n(t) \equiv \frac{\eta_n(t) - \eta_0(t)}{\eta_1(t)}. \quad (3.3)$$

Equation (3.2) is an ordinary differential equation of the first order of the form

$$dx/dt = f(x, t). \quad (3.4)$$

The following existence and uniqueness theorem is known for such equations.⁵

Suppose $f(x, t)$ and $\partial f(x, t)/\partial x$ exist and are continuous in a $t-x$ domain D (open set). Suppose the point (t^0, x^0) is contained in D . Then there exists a unique solution, $x = X(t)$, in D and on some interval I of t which contains the point t^0 such that $x^0 = X(t^0)$.

In our equation we note that on the interval I the coefficients $a_k(t)$ are continuous, and we suppose $\tilde{\eta}_n(t)$ is finite on a subset I' of I . Then the right-hand side of (3.2) exists and is continuous on I' . Since $f_n(\tilde{\eta}_n, t)$ is a polynomial in $\tilde{\eta}_n$, it follows that $\partial f_n(\tilde{\eta}_n, t)/\partial \tilde{\eta}_n$ also exists and is continuous on I' . Therefore, a solution of (3.2) exists which is unique on I' . We note, also, that the first $n+1$ terms of (2.1) are reproduced. That $\tilde{\eta}_n(t)$ is a continuous function of the initial conditions can be proved similarly from the same hypotheses of the existence and uniqueness theorem.

Using the existence and uniqueness properties, we find that the approximation scheme gives a unique solution. Of consequence, therefore, is the fact that two different solutions of (3.2) will not cross on I' .

As previously mentioned, the constant of integration is determined by a knowledge of the exact value of $\tilde{\eta}(t, g)$ at one point, $t = t_0$. If $\tilde{\eta}(t_0; g)$ is a monotonically increasing (decreasing) function of g , it then follows from the uniqueness of the solution, that to any order n , if $t_0 \in I'$, the solution $\tilde{\eta}_n(t)$ is similarly a monotonically increasing (decreasing) function of g for any $t \in I'$. Also since $\tilde{\eta} \equiv 0$ is a solution, if $\tilde{\eta}(t_0; g)$ is positive (negative), then $\tilde{\eta}_n(t)$ will be positive (negative) for $t \in I'$.

To summarize, the n th-order improved solution $\tilde{\eta}_n(t)$ has the following properties:

- (a) Optimizes convergence,
- (b) Reproduces at least the first $n+1$ coefficients of (2.1); hence,

$$\lim_{n \rightarrow \infty} \tilde{\eta}_n(t) = \tilde{\eta}(t) \equiv \tilde{\eta}(t; g);$$

(c) Is a monotonically increasing (decreasing) function of g .

(d) Is positive (negative) definite.

From properties (b) and (c) it must not be concluded that the exact result $\tilde{\eta}(t; g)$ is monotonically increasing (decreasing) for all t . The reason is that $f(\tilde{\eta}, t)$ may cease to be regular near some points, e.g., near a branch point; thus the hypotheses of the uniqueness theorem are not satisfied on the whole range of interest of the variable t . Some of these singularities are connected with the existence of a singular solution (the envelope) of Eq. (3.1). In this language, property (c) states that the family of solutions of (3.2) does not possess an envelope. Of course, this will be true for the exact solution if and only if $f(\tilde{\eta}, t)$ and $\partial f(\tilde{\eta}, t)/\partial \tilde{\eta}$ exist and are continuous. In general, these properties are not supposed or known from the original series (2.1). The approximation scheme is, therefore, better suited for regions where the functions to be approximated are known beforehand to possess a monotonically increasing (decreasing) behavior. This limitation was apparent in the inversion of the series (2.1) which holds only if $\partial \eta / \partial g \neq 0$.

IV. APPLICATION TO MOLECULAR MODELS

The technique developed in the preceding sections is applied to the virial expansion of several models of interest, with η being the variable P/kT and the real parameter, g , being the density, ρ . One hopes that the behavior of the improved solution for η may yield a better understanding of the nature of possible phase transitions of the model. It should be made clear, however, that the present approach assumes the virial coefficients to be *independent* of the density (volume). This assumption, then, becomes an integral part of the n th-order improved solution. Therefore, any shortcomings inherent in such a basic assumption will be reflected in our solution.

A phase transition will be determined by a discontinuity in the function $\eta(\rho)$, or any one of its derivatives.⁶ A discontinuity in $\eta(\rho)$ is defined as a first-order phase transition; a discontinuity in $\partial \eta(\rho) / \partial \rho$ [with $\eta(\rho)$ continuous] corresponds to a second-order phase transition, etc.

The density ρ is determined by the *exact* value of η at some point $t = t_0$. Since all exact solutions are monotonically increasing functions of the density, the improved solution will be, similarly, monotonically increasing in ρ (this has been proved rigorously by Van Hove⁷ for an intermolecular force of finite range and with a hard core).

From the derivation (Sec. II), it is clear that the region of low density will be reproduced by the im-

⁵ E. A. Coddington and N. Levinson, *Theory of Ordinary Differential Equations* (McGraw-Hill Book Company, Inc., New York, 1955), Chap. 1.

⁶ J. E. Mayer, *J. Chem. Phys.* **16**, 665 (1948). J. E. Mayer and S. F. Streeter, *J. Chem. Phys.* **7**, 1019 (1939).

⁷ L. Van Hove, *Physica* **15**, 951 (1949).

proved solutions *irrespective* of the boundary condition set on the basic differential equation (2.5). In other words, properties (a) and (b) (of Sec. III) are independent of the boundary condition, whereas properties (c) and (d) depend on it.

To study the connection between the behavior of the improved solution to that of the actual system, one may consider the following: Suppose there exists an analytical continuation of the function $\eta(\rho)$ valid outside of the radius of convergence of the virial series. The n th-order improved solution converges in this region and, further, it reproduces the first n virial coefficients. Hence in the limit that n becomes infinite, the improved solution is indeed the analytic continuation of $\eta(\rho)$. As such, the improved solution will represent the physics of the model and its properties, e.g., discontinuities in the function or its derivatives will represent the "physical" phase transitions of the model.

A. Herzfeld-Mayer Model

This model⁸ consists of a one-dimensional system of hard lines of length σ . The equation of state is given by the virial expansion

$$P/kT = B_1(\sigma)\rho + B_2(\sigma)\rho^2 + \dots, \quad (4.1)$$

where

$$B_n(\sigma) = \sigma^{n-1}, \quad n \geq 1.$$

Substituting the coefficients $B_n(\sigma)$ into (2.5) yields the differential equation

$$d\eta/d\sigma = \eta^2; \quad (4.2)$$

i.e., $a_k(\sigma) \equiv 0$ for $k \geq 3$ in (3.1). The initial condition for (4.2) is

$$\eta = \rho \quad \text{for} \quad \sigma = 0. \quad (4.3)$$

The solution of (4.2) with the boundary condition (4.3) is

$$\eta = \frac{\rho}{1 - \sigma\rho}, \quad (4.4)$$

which is the exact result of this model. In general, the second-order improved solution can be obtained directly and is given by

$$\eta = \eta_0 + \frac{\eta_1}{K - \eta_2/\eta_1}, \quad (4.5)$$

where K is an integration constant. The connection between K and the original parameter g can be obtained when the limit of (4.5) as $g \rightarrow 0$ is considered. It follows that $K \rightarrow 1/g$ as $g \rightarrow 0$, in which case the first two terms of the original series are recovered (as promised in summary (b) of Sec. III).

The results show that the second-order improved solution is the exact solution of the Herzfeld-Mayer model and, thus, gives us an insight into the nature of the improved solution. In the context of this technique,

⁸ K. F. Herzfeld and M. G. Mayer, *J. Chem. Phys.* **2**, 38 (1934).

the Herzfeld model is the analog in statistical mechanics of N - θ scattering in the Lee model of field theory.⁹

B. Two-dimensional Lattice Gas

A model which has been considered in studying the effects of the strongly repulsive cores of atoms in real fluids is that of the two-dimensional lattice gas of hard squares. In this model, which is equivalent to an Ising model in a magnetic field,¹⁰ the "atoms" are restricted to lie on the sites of a simple quadratic lattice. Only nearest-neighbor interactions are considered, and multiple occupancy of sites is prohibited by an infinite repulsive potential.

Such a model yields the following virial coefficients:

$$\begin{aligned} B_1 &= 1, \quad B_2 = \frac{1}{2}(1 - 4f'), \quad B_3 = \frac{1}{3}(1 + 12f'^2), \\ B_4 &= \frac{1}{4}(1 - 12f'^2 - 40f'^3 - 12f'^4), \\ B_5 &= \frac{1}{5}(1 + 80f'^3 + 220f'^4 + 160f'^5), \end{aligned} \quad (4.6)$$

where

$$f' \equiv e^{-V_0/kT} - 1, \quad (4.7)$$

and V_0 is the potential energy between nearest-neighbors ($0 < f' < \infty$ denotes attractive, $-1 < f' < 0$ represents repulsive interaction).

Substituting the coefficients (4.6) into the basic differential equation (2.5) gives

$$\begin{aligned} d\eta/df' &= -2\eta^2 + 2\eta^3 + (-7/6 + 2f' - 6f'^2 - 12f'^3)\eta^4 \\ &+ (\frac{1}{2} - 4f' + 24f'^2 + 80f'^3 + 52f'^4)\eta^5 + \dots \end{aligned} \quad (4.8)$$

The density of the system is introduced in the boundary condition of Eq. (4.8) which is

$$\eta = -\ln(1 - \rho) \quad \text{for} \quad f' = 0. \quad (4.9)$$

Hence, our method for determining the constant of integration introduces the proper limiting behavior of the improved solution (to the ideal lattice gas in this case) in quite a natural manner.

In the n th-order improved solution, the first $n-1$ derivatives with respect to f' , evaluated at $f'=0$, are exact. [Recall that since $\eta(0) = -\ln(1-\rho)$, then in $[\eta(0)]^k$ for $k \leq n$ only terms up to ρ^n can be kept.] This is a statement of property (b), and, as a consequence, the solution reproduces the exact virial coefficients B_1, B_2, \dots, B_n . To determine the "predicted" higher virial coefficients $B'_{n+1}, B'_{n+2}, \dots$, derivatives of order greater than n are necessary. However, the derivatives of order higher than n break down *before* the function $\eta(f)$ or its first $n-1$ derivatives. (See Ref. 3, footnote 11) Therefore, the "predicted" virial coefficients $B'_{n+1}, B'_{n+2}, \dots$, do not have the same convergence properties as the improved solution and should not be used to study the convergence of the latter.

⁹ See, for example, M. S. Maxon and R. B. Curtis, *Phys. Rev.* **137**, B996 (1965), Eq. (53).

¹⁰ T. D. Lee and C. N. Yang, *Phys. Rev.* **87**, 410 (1952).

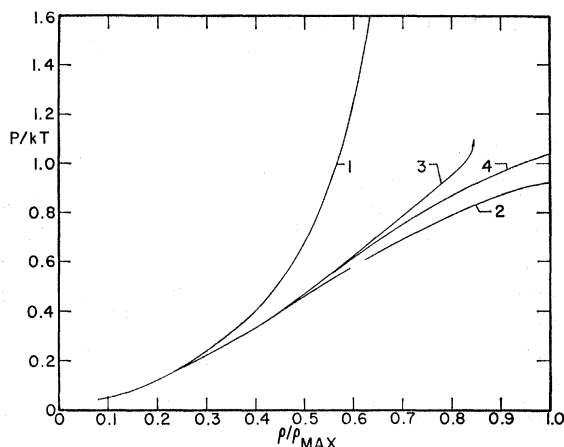


FIG. 1. Simple quadratic lattice ($f' = -1$), pressure versus density. 1 designates the second-order improved solution (which reproduces the first two virial coefficients), etc.

It is interesting to find that our third-order improved solution can be obtained in closed form:

$$\frac{1}{\eta} + \ln \left[1 - \frac{1}{\eta} \right] = 2f' - \frac{1}{\ln(1-\rho)} + \ln \left[1 + \frac{1}{\ln(1-\rho)} \right], \quad (4.10)$$

where condition (4.9) has been used to eliminate the constant of integration.

Solution (4.10) has the property

$$\eta = 1 \quad \text{for} \quad \rho = 1 - e^{-1}, \quad (4.11)$$

irrespective of the value of f' . This behavior was anticipated as $\eta \equiv 1$ is a solution, and the boundary condition (4.9) requires $\rho = 1 - e^{-1}$. However, from this it should not be concluded that different isotherms cross at $\rho = 1 - e^{-1}$. The requirement that they do not cross $(\partial P / \partial T)_\rho \geq 0$, is equivalent to

$$\eta \geq (1 + f') \ln(1 + f') d\eta / df', \quad (4.12)$$

which is satisfied. Further, it is trivial to show that (4.10) reproduces the first three coefficients of the virial expansion.

The different improved solutions were considered only for negative values of f' (repulsive interactions). The study of the region $f' > 0$ requires the use of additional virial coefficients and will be left to a future investigation.

Figure 1 shows the first four improved solutions for the case of hard squares ($f' = -1$). The sequence of approximations shows a rather rapid rate of convergence for large values of ρ / ρ_{\max} . The odd-order improved solutions are finite. However, the even-order improved solutions have a singularity; e.g., the second-order improved solution has a simple pole at

$$\rho / \rho_{\max} = 2(1 - e^{-1/2}) = 0.787.$$

The existence of singularities in the n th-order improved solution can be determined by the sign of its corresponding $a_n(f')$ coefficient in the differential equation. If $a_n(f')$ is negative (positive) for a certain range of negative (positive) values of f' , then singularities can exist for that range of values of f' .

Gaunt and Fisher¹¹ made use of 13 terms of the activity and virial series at low density and nine terms of the appropriate high-density expansion in conjunction with the Padé approximation to predict a continuous (or "second-order") transition to an ordered state at $\rho = (0.740 \pm 0.008) \rho_{\max}$.

The dotted curve in Fig. 2 shows their [5,6] Padé approximant for the low-density expansion and the [4,4] Padé approximant for the high-density region.

Our fifth-order improved solution is also shown in Fig. 2 and agrees quite well with the result of Gaunt and Fisher; however, it does not reproduce the region where the transition is supposed to occur. Our next approximations will be quite relevant in determining the existence and nature of the transition.

C. Fisher Model

The study of this model¹² elucidates our technique when second-neighbor interactions are considered. Furthermore, such a study allows for a comparison of our approximation results with an exact result at one particular temperature.

The hard square model ($f' = -1$) of part B is altered by the addition of a second-neighbor interaction across alternate squares (this we call the "Fisher Model"), and

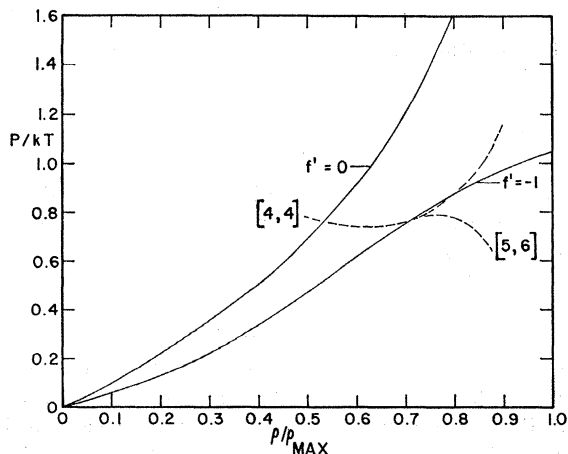


FIG. 2. Comparison of the fifth-order improved solution (which reproduces the first five virial coefficients) with the [5,6] low-density and the [4,4] high-density Padé approximants of Fisher and Gaunt. The curve labeled $f' = 0$ represents the initial boundary condition, $P - kT = -\ln[1 - (\rho / \rho_{\max})]$.

¹¹ D. S. Gaunt and M. E. Fisher, King's College, London unpublished report.

¹² M. E. Fisher, J. Math. Phys. 4, 278 (1963).

the following virial coefficients are obtained:

$$\begin{aligned} B_2 &= 5/2 - f, & B_3 &= 13/3 - 4f + 2f^2, \\ B_4 &= 17/4 - 9f + (21/2)f^2 - 5f^3, \end{aligned} \quad (4.13)$$

$$B_5 = -19/5 - 8f + 28f^2 - 32f^3 + 14f^4,$$

where

$$f = e^{-V/kT} - 1, \quad (4.14)$$

and V is the potential energy between second neighbors.

The basic differential equation is found to be

$$\begin{aligned} d\eta/df = & -\eta^2 + (1+2f)\eta^3 + (-19/12 - 4f - 4f^2)\eta^4 \\ & + (25/4 + (13/2)f + 12f^2 + 8f^3)\eta^5 + \dots \end{aligned} \quad (4.15)$$

The initial condition for the differential equation (4.15) is determined by matching the n th-order improved solution at $f=0$ with the n th-order improved solution of (4.8) at $f'=-1$. This prescription for determining the constant of integration, with η a function of two variables, can be generalized easily to the case that η is a function of several variables, t_1, \dots, t_k . Here we are assuming that the exact solution η is known only at one single point in the t -space ($f' = f = 0$ for the present model, which reduces to the ideal lattice gas). In cases where the exact η is known at several points (or regions), these values of the exact η can be incorporated, in a straightforward way, into the improved solution.

The fifth-order improved solutions (keeping terms including B_5) for various values of f are shown in Fig. 3. The case when $f=1$, $f'=-1$ agrees with the exact result of Fisher only up to $\rho/\rho_{\max} \approx 0.4$. Again, as in the lattice gas in Sec. IVB the case with $f > 0$ (attractive) seems to require considerably more virial coefficients. The bottom curve represents the results obtained by considering the case $f=f'=-1$ and is the so-called dimer model.

Figure 4 shows the first four improved solutions of the dimer problem ($f=f'=-1$; $\rho_{\max}=1/3$). The fifth-order improved solution, in contrast to the first three

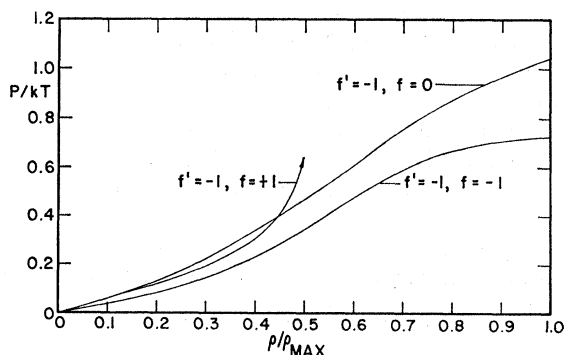


FIG. 3. Dimer model ($f'=-1$, $f=-1$; $\rho_{\max}=1/3$) and Fisher model ($f'=-1$, $f=+1$; $\rho_{\max}=1/2$), pressure versus density. The curve labeled $f'=-1$, $f=0$ represents the initial boundary condition and is the curve labeled 4 in Fig. 1.

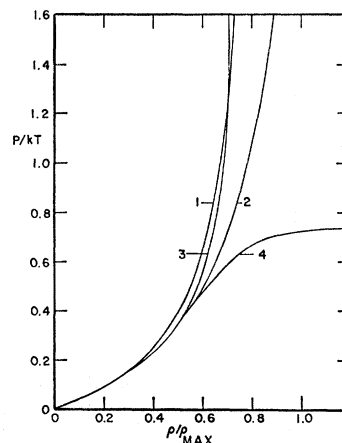


FIG. 4. Dimer model ($f'=-1$, $f=-1$; $\rho_{\max}=1/3$), pressure versus density. 1 designates the second-order improved solution (which reproduces the first two virial coefficients), etc.

approximations, is finite and this may be an indication of a phase transition. However, the actual existence of it and its nature requires higher approximations.

D. Hard Spheres

This model has received considerable attention, since it is the most unsophisticated continuous model representing the property of impenetrability exhibited by atoms and molecules in real gases. However, no satisfactory solution is known for it except results derived mainly by simplifying the model still further to that of a hard lattice gas.

Here, the system of hard spheres is investigated directly with the present approximation scheme. The first five virial coefficients obtained by Hiroike¹³ and by Katsura and Abe¹⁴ yield the following differential equation:

$$\begin{aligned} d\eta/df = & -\eta^2 - [2f + 1.875f^2]\eta^3 \\ & + [-5f^2 - 10.7606f^3 - 7.0835f^4 - 0.9504f^5]\eta^4 \\ & + [-14f^3 - 49.4772f^4 - 69.912931f^5 \\ & - 46.64403f^6 - 15.179432f^7 - 2.735406f^8 \\ & - 0.23594f^9]\eta^5 + \dots, \end{aligned} \quad (4.16)$$

where

$$f = e^{-\epsilon/kT} - 1, \quad (4.17)$$

and ϵ is the constant potential energy. f is positive (negative) when the potential is attractive (repulsive).

The boundary condition for (4.16) is

$$\eta = \rho \quad \text{for } f = 0. \quad (4.18)$$

The solutions of (4.16) evaluated at $f=-1$ for different values of the boundary condition (4.18) are shown in Fig. 5. The straight line has slope $2\pi\sqrt{2/3}$ and corresponds to the boundary condition at $f=0$. The specific value of the slope follows from the following

¹³ K. Hiroike, J. Phys. Soc. Japan 12, 326 (1957).

¹⁴ S. Katsura and Y. Abe, J. Chem. Phys. 39, 2068 (1963).

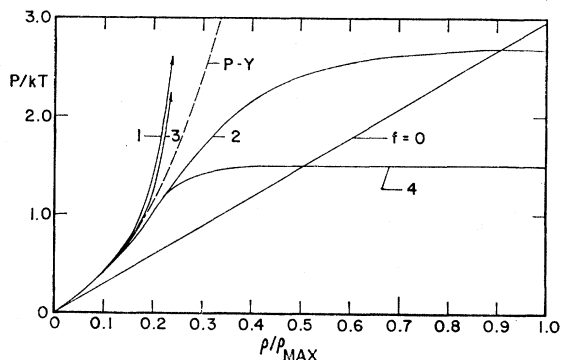


FIG. 5. Hard-sphere gas [$f = -1$; $\rho_{\max} = (2\pi/3)\sqrt{2}$], pressure versus density. 1 designates the second-order improved solution (which reproduces the first two virial coefficients), etc. The curve denoted by $f=0$ represents the boundary condition, $P/kT = \rho$. The dashed curve represents the result of the scaled-particle theory [see Eq. (4.20)].

normalization:

$$b \equiv \frac{2\pi}{3} \sigma^3 = 1, \quad (4.19)$$

where σ is the sphere diameter.

Again, as in the case of the hard squares of Sec. B, the even-(odd-) order improved solutions are singular (finite), e.g., the second-order solution has a simple pole at $\rho/\rho_{\max} = 3/2\pi\sqrt{2}$. However, in contrast to the results for the lattice gas, the even and odd solutions seem to be converging to *different* solutions.

It is possible from the outset to consider the case $f = -1$ and to use the dimension of the hard sphere [the variable b in Eq. (4.19) for example] as the continuous variable.¹⁵ We can then use the six virial coefficients which are known for the case of hard spheres and disks to obtain the basic differential equation (3.1).¹⁶ The same behavior was found for the even- and odd-order solutions, i.e., the even-order solutions become infinite for some value of $\rho/\rho_{\max} \approx (\rho/\rho_{\max})^*$ and the odd-order solutions become essentially constant for $(\rho/\rho_{\max}) \gtrsim (\rho/\rho_{\max})^*$.

It seems that the qualitative behavior of the improved solution resembles that conjectured by Mayer in his theory of condensation.¹⁷ However, one cannot completely rule out the possibility that a further approximation may give a result in between the two limiting behaviors of the even- and odd-order solutions. Such has been obtained by others. For example, the curve labeled $P-Y$ in Fig. 5 refers to the solution of the three-dimensional Percus-Yevick equation for hard

spheres¹⁸:

$$\eta = [4\alpha(1+\alpha+\alpha^2)/(1-\alpha)^3], \quad (4.20)$$

where

$$\alpha \equiv \frac{\pi}{3\sqrt{2}} \rho / \rho_{\max}.$$

This is the same equation of state as that obtained¹⁹ from the scaled-particle model. Moreover, result (4.20) is in agreement with molecular dynamics²⁰ and Monte Carlo²¹ calculations of the equation of state for hard spheres at densities below the phase transition obtained by these computer results.

V. SUMMARY AND DISCUSSION

Using the virial expansion together with the improved convergence scheme of Sec. II, successive numerical approximations are obtained for the equation of state of a thermodynamic system. Two exact features of the improved scheme are of interest: pressure is a monotonically increasing function of the density, and the solution reproduces the virial coefficients which are used.

The solution for a one-dimensional system of hard rods is obtained exactly in this scheme. For the two-dimensional hard-square lattice gas, the results agree quite well, up to the phase transition, with the recent Padé approximant results (at low and high density) of Gaunt and Fisher. Our next approximations should be relevant to the existence and nature of this transition. Since the result for the hard-square lattice is used as the boundary condition for the Fisher and dimer model, the appearance of the "second-order" phase transition in the Fisher model, as well as a possible phase transition in the dimer problem, may be connected with the appearance first of a transition in the hard-square lattice gas.

For the system of hard spheres, the qualitative behavior of the improved solution resembles that conjectured by Mayer in his theory of condensation.

In summary, the results obtained indicate that this new approximation scheme is predicting correctly the behavior of the "gas" under consideration. This is attained by using only a few terms of the virial series. Future work (evaluating and using more terms) will yield more definite statements regarding phase transitions. Other thermodynamic variables may be studied also by this scheme. In addition, the extension of this

¹⁸ M. S. Wertheim, *J. Math. Phys.* **5**, 643 (1964).

¹⁹ H. Reiss, H. L. Frisch, and J. L. Lebowitz, *J. Chem. Phys.* **31**, 369 (1959).

²⁰ B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **27**, 1208 (1957).

²¹ W. W. Wood and J. D. Jacobson, *Proceedings of the Western Joint Computer Conference, San Francisco Institute of Radio Engineers, New York 1959*, p. 261 (unpublished); W. W. Wood, F. R. Parker, and J. D. Jacobson, *Nuovo Cimento Suppl.* **9**, 133 (1958).

¹⁵ M. Alexanian and D. E. Wortman, Lawrence Radiation Laboratory, University of California, Report No. UCRL 12473, (unpublished).

¹⁶ F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**, 939 (1964).

¹⁷ J. E. Mayer, *J. Chem. Phys.* **5**, 67 (1937). For further references, see C. N. Yang and T. D. Lee, *Phys. Rev.* **87**, 404 (1952).

method to multicomponent systems should warrant further investigation. Hence, it is hoped that this new approximation scheme will be quite useful in the field of statistical mechanics.

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Effect of Normal-Fluid Motion on Third Sound in Liquid-Helium Films

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Some theoretical consequences are derived of a proposed viscous force on the normal-fluid component of the He II film. In contrast with earlier calculations, in which the normal fluid was assumed to be immobile, this new assumption allows large energy attenuations, such as have recently been observed in third sound in He II films and in a wave mode of He II partially clamped in narrow channels. Atkins's three equations describing third sound are modified to take account of energy and entropy transfer associated with normal-fluid motion, and wave modes are obtained which simultaneously satisfy these equations and the normal-fluid equation of motion with a viscous force $-Rv_n$. The four wave variables are: ξ and T' , respectively, the local fluctuations in film thickness and temperature, and v_s and v_n , the superfluid and normal-fluid velocities. Attenuation and velocity of the wave mode corresponding to third sound are calculated at temperatures from 1.2°K through T_λ for all values of the dimensionless viscosity coefficient ($R/\omega\rho$). The maximum calculated attenuation varies from 0.47 cm⁻¹ at 1.2°K to 17.3 cm⁻¹ at 2.1°K; at the lower temperature the observed attenuation is about 2 cm⁻¹. However, the anomalously rapid decrease in velocity of third sound observed by Everitt *et al.* could not be explained in this manner. Evidence for normal-fluid motion in the film is presented, and some feasible experiments for detecting it are described.

INTRODUCTION

THE discovery that liquid helium at temperatures below its λ point can flow in a thin film out of a containing vessel is almost 30 years old.¹ Many elegant experimental and theoretical investigations have since been carried out on the He II film, but many problems remain.² Recently, such investigation has been reported by Atkins³ and Everitt *et al.*⁴ These workers examined, respectively in theory and experiment, third sound, i.e., surface waves on the film. It was found that if only superfluid motion is allowed, the surface waves should be unattenuated and have a characteristic velocity, $u_3(T)$. The observed waves showed appreciable attenuations and had velocities up to 20% lower than expected. This paper presents a supplementary, more complete, theory of two-fluid flow in the film. We will consider what modifications are necessary if, in addition to free superfluid motion, viscous normal-fluid motion is as-

sumed. Some consequences of this additional assumption will be examined, and it will be shown that the observed attenuation of third sound can be explained, at least qualitatively.

The role of normal-fluid motion in frictional dissipation of energy associated with *macroscopic* flow of the He II film has also been of continued interest. In addition, interest has recently quickened in the related problems of He II flow through small orifices and channels. In this kind of flow, the superfluid is much more mobile than the normal fluid, but energy cannot be lost to the superfluid unless its velocity exceeds some critical value.⁵ Dissipative effects in small-channel flow of He II therefore draw attention to the normal-fluid motion. Experiments and theories of this kind have a unique property: In most experiments on He II large normal-fluid effects obscure small superfluid effects, but in these experiments the roles of the fluids are interchanged.

Several recent investigations bear directly on the problem of wave motion in liquid helium with fully or partially immobilized normal fluid. Pellam⁶ first showed that if a viscous drag, of the form $-Rv_n$ in which v_n is the normal-fluid velocity, on the normal fluid were superposed on the usual two-fluid thermohydrodynamic

* Present address.

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² K. R. Atkins, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1957), Vol. II.

³ K. R. Atkins, *Phys. Rev.* **113**, 962 (1959).

⁴ C. W. F. Everitt, K. R. Atkins, and A. Denenstein, *Phys. Rev.* **136**, A1494 (1964).

⁵ R. P. Feynman, in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1955), Vol. I.

⁶ J. R. Pellam, *Phys. Rev.* **73**, 608 (1948).