

Solution of a truncated Kirkwood-Salsburg equation for the hard-sphere gas

Robert H. Swendsen

Institut für Festkörperforschung, Kernforschungsanlage Jülich, Jülich, Germany

William Klein

Institut für Theoretische Physik der Universität zu Köln, Cologne, Germany

(Received 18 August 1975)

A truncated form of the Kirkwood-Salsburg equation for the hard-sphere gas is solved. An exact algebraic recurrence relation is obtained for the coefficients of an expansion of the two-particle correlation function in powers of the activity, z , in the neighborhood of $z=0$. The methods of series analysis and Padé approximants allow this solution to be extended to all $z \in [-1, 11.6048]$. An equation of state is obtained which reproduces the first three virial coefficients exactly and shows a phase transition at $z=11.6048$, which appears to be weakly second order. It is demonstrated that minor modifications of the integral equation could substantially alter the analytic structure of the solution.

I. INTRODUCTION

Although the hard-sphere gas has been extensively studied¹ by both computer simulation² and truncation of exact hierarchies of equations for the distribution functions,³⁻⁷ a complete description of its thermodynamic properties has not been obtained. Computer simulations have convincingly demonstrated the existence of a first-order fluid-solid phase transition,² but they appear to be incapable of determining the nature of the singularity at the phase transition or the mechanism for symmetry breaking.

The solution of truncated hierarchies has met with varying success. Generally, the truncations are not systematically improvable and, in most cases, even the truncated equations cannot be solved exactly. The first Percus-Yevick equation is an exception to this last statement, but the solution fails to show a phase transition.^{5,6}

In this paper, we present the solution to an integral equation for the pair-distribution function, which was obtained by truncating the Kirkwood-Salsburg equation⁸

$$\rho_2(\vec{x}_1, \vec{x}_2) = z(1 + f_{12}) \left(\rho_1(\vec{x}_2) + \int \rho_2(\vec{x}_2, \vec{x}_3) f_{13} d\vec{x}_3 \right), \quad (1)$$

where

$$z = e^{\mu/k_B T} / \lambda^3, \quad (2)$$

$$\lambda = h / (2\pi m k_B T)^{1/2}; \quad (3)$$

f_{ij} is the Mayer function

$$f_{ij} = \exp[-\phi(\vec{x}_i - \vec{x}_j)/k_B T] - 1, \quad (4)$$

and ϕ is the two-particle potential. For the hard-sphere gas,

$$f_{ij} = \begin{cases} -1, & |\vec{x}_i - \vec{x}_j| < \sigma, \\ 0, & |\vec{x}_i - \vec{x}_j| > \sigma, \end{cases} \quad (5)$$

with σ being the diameter of the hard spheres. Equation (1) was derived by Sabry,⁹ using a physical approximation, and by one of the authors as the first-order contribution to a perturbative expansion.¹⁰ The second derivation has the advantages of being systematically improvable and of showing that all contributions to $\rho_2(\vec{x}_1, \vec{x}_2)$ can be obtained by solving Eq. (1) with different inhomogeneous terms. This last property suggests that the structure of Eq. (1) may have an importance far beyond that of the specific approximation which it represents.

We have expanded the solution to Eq. (1) in powers of z and have obtained an exact recurrence relation, which involves only algebraic operations. Using this recurrence relation, we have generated all coefficients up to the 50th power in z , to about 30 significant digits. The length of the resulting series enabled us to apply the methods of series analysis very effectively to obtain both the analytic properties of the solution and numerical values to essentially arbitrary accuracy.¹¹

From the solution to Eq. (1) we have obtained an approximate equation of state for the hard-sphere gas, which correctly reproduces the first three virial coefficients and exhibits a phase transition. Unfortunately, the phase transition occurs at a density of 27% close-packing (as opposed to value of 63% close-packing given by computer simulation) and predicts a divergence of the isothermal compressibility, which would be characteristic of a second-order transition. On the other hand, the

divergence is weak and we shall present evidence that a modification of the inhomogeneous term in Eq. (1) might be capable of describing a first-order transition.

II. METHOD OF SOLUTION

Since we are interested in a solution to Eq. (1) in the gas, all distribution functions are invariant under arbitrary translations and rotations. $\rho_1(\vec{x}_2)$ is then independent of \vec{x}_2 and is equal to the average density ρ . Furthermore, $\rho_2(\vec{x}_1, \vec{x}_2)$ is a function only of the distance between the points \vec{x}_1 and \vec{x}_2 , and we shall introduce the notation

$$\vec{x}_{12} = \vec{x}_2 - \vec{x}_1, \quad x_{12} = |\vec{x}_{12}|. \quad (6)$$

It will also prove convenient to introduce a unit of length such that the exclusion sphere has unit volume:

$$\frac{4}{3} \pi \sigma^3 = 1. \quad (7)$$

As a first step, we shall simplify the inhomogeneous term in Eq. (1) by defining the function

$$\bar{\rho}_2(x_{12}) = \rho_2(x_{12}) - z\alpha, \quad (8)$$

where

$$\alpha = \rho/(1+z), \quad (9)$$

so that Eq. (1) takes the form

$$\bar{\rho}_2(x_{12}) = z\alpha f_{12} + z(1+f_{12}) \int \bar{\rho}_2(x_{23}) f_{13} d\vec{x}_{23}. \quad (10)$$

As the solution of this equation has been shown to be analytic in the neighborhood of $z=0$,¹² we can expand the solution to Eq. (10) as a power series in z ,

$$\bar{\rho}_2(x_{12}) = z\alpha f_{12} + \alpha(1+f_{12}) \left(\frac{\sigma}{x_{12}} \right) \sum_{-1}^{\infty} P_n(x_{12}) (\pi\sigma^3)^n z^{n+1}, \quad (11)$$

where some factors have been explicitly removed from the expansion coefficients.

Upon substitution in Eq. (10) and equating powers of z , we find the recurrence relation

$$P_n(x_{12}) = x_{12} (\pi\sigma^3)^{-1} \int x_{23}^{-1} (1+f_{23}) f_{13} P_{n-1}(x_{23}) d^3x_3, \quad (12)$$

for which the first coefficient is given by

$$P_1(x_{12}) = (\pi\sigma^4)^{-1} x_{12} \int f_{13} f_{23} d^3x_3. \quad (13)$$

The integral in Eq. (13) is the volume of overlap of two spheres of radius σ whose centers are a distance x_{12} apart, and is clearly zero for $x_{12} > 2\sigma$. After the angular integrations have been per-

formed,

$$P_1(x_{12}) = 2\pi x_{12} (\pi\sigma^4)^{-1} \int_{x_{12}-\sigma}^{\sigma} y h(x_{12}, y) dy, \quad (14)$$

where

$$h(x, y) = \frac{1}{2} [(x-y)^2 - \sigma^2], \quad (15)$$

and the final integral is trivial.

The recurrence relation (12) involves exactly the same angular integration and can be written as

$$P_n(x_{12}) = 2(\pi\sigma^3)^{-1} \int_{\max(\sigma, x_{12}-\sigma)}^{\min(n\sigma, x_{12}+\sigma)} h(x, y) P_{n-1}(y) dy, \quad (16)$$

with the provision that P_n is zero unless the upper limit of integration is greater than the lower limit (overlap volumes are always positive), i.e., $x_{12} < (n+1)\sigma$. This condition leads to discontinuities in the derivatives of $\rho_2(x_{12})$ as a function of x_{12} at the points $x_{12} = n\sigma$. This property, combined with the explicit form of P_1 , Eqs. (14) and (15), suggests expressing P_n in the form of polynomials $\{P_n^m(x_{12}), x_{12} \in [m\sigma, (m+1)\sigma]\}$, and expressing P_n^m as a function of the new variables

$$\bar{x}_m = (x_{12} - m\sigma)/\sigma \quad (17)$$

so that $\bar{x}_m \in [0, 1]$. The recurrence relation (12) then becomes

$$P_n^m(\bar{x}_m) = \sum_{l=1}^{n-1} \int_{\max(0, \bar{x}_m - l + m)}^{\min(1, \bar{x}_m + 1 - l + m)} \bar{h}_{l-m}(\bar{x}_m, y_l) P_{n-1}^l(\bar{y}_l) d\bar{y}_l, \quad (18)$$

where

$$\begin{aligned} \bar{h}_{l-m}(\bar{x}_m, \bar{y}_l) &= 2\sigma^{-2} h(\sigma(\bar{x}_m + m), \sigma(\bar{y}_l + 1)) \\ &= [\bar{x}_m - \bar{y}_l - (l-m)]^2 - 1. \end{aligned} \quad (19)$$

If we consider the condition that the upper limit of integration must be greater than the lower limit, we see that the only values of l which make a non-zero contribution are $m-1$, m , and $m+1$. Again, from the conditions under which P_{n-1}^l is nonzero, we only get contributions from these terms when

$$\begin{aligned} m &\leq n-2 \quad \text{for } l=m+1, \\ m &\leq n-1 \quad \text{for } l=m, \\ m &\geq 2 \quad \text{for } l=m-1. \end{aligned} \quad (20)$$

To explicitly perform the remaining integrals over polynomials in \bar{y}_l and put the recurrence relation in a form suitable for numerical evaluation, we define the expansion coefficients $Q(n, m, l)$ so that

$$P_n^m(\bar{x}_m) = \sum_{l=1}^{3n+2} Q(n, m, l) (\bar{x}_m)^l \quad (21)$$

and $Q(n, m, l) = 0$ when the conditions (20) are not satisfied. With the coefficients $H_s(i, j)$ defined so that

$$\bar{h}_s(x, y) = \sum_{i=1}^s \sum_{j=1}^s H_s(i, j) x^i y^{s-j}, \quad (22)$$

the final recurrence relation takes the form

$$Q(n, m, l) = \sum_{k=1}^{3n-1} \sum_{i=1}^3 \sum_{j=1}^3 (k+j-1)^{-1} [H_1(i, j) Q(n-1, m+1, k) \delta_{i, i+j+k-1} + H_0(i, j) Q(n-1, m, k) \delta_{i, i} + H_{-1}(i, j) Q(n-1, m-1, k) (\delta_{i, i} - \delta_{i, i+j+k-1})]. \quad (23)$$

This expansion involves only algebraic operations, which are easy to perform rapidly and to a high accuracy on the computer. We have obtained all coefficients up to $n = 50$ for all values of m and l to an accuracy of better than 30 significant digits. The final expression for $\rho_2(x_{12})$ can now be written as

$$\rho_2(x_{12} \in [m\sigma, (m+1)\sigma]) = \frac{z\rho}{1+z} (1+f_{12}) \left[1 + \frac{\sigma}{x_{12}} z \sum_{i=1}^{3n+2} S_{mi}(z) \left(\frac{x_{12}}{\sigma-m} \right)^{i-1} \right], \quad (24)$$

where the functions $S_{mi}(z)$ are defined as

$$S_{mi}(z) = \sum_{n=1}^{\infty} Q(n, m, l) (\pi\sigma^3)^n z^{n-1}. \quad (25)$$

III. ANALYTIC PROPERTIES OF THE SOLUTION

Since we have obtained a large number of coefficients to a very high accuracy, the methods of series analysis can be directly applied to find the analytic properties of the function $S_{mi}(z)$ with a high level of confidence in the validity of the results. In addition, the investigation of the analytic properties of these functions is aided by a proof¹² that the solution to Eq. (1) is analytic in z as long as

$$1 - z\hat{f}(k) \neq 0, \quad (26)$$

where $\hat{f}(k)$ is the Fourier transform of f_{12} , and takes the form

$$\hat{f}(k) = (4\pi/k^2) [\sigma \cos(k\sigma) - (1/k) \sin(k\sigma)]. \quad (27)$$

The closest possible critical values of z then occur at -1 and 11.6048 .

The direct application of the ratio method to the expansions of the functions $S_{mi}(z)$ and extrapolation of the results with the use of Neville tables confirms the existence of a nonanalyticity at -1 and shows it to be a square-root branch point for all values of m and l . If the branch point is unfolded by using the transformation

$$z = z_c [1 - (1 + \zeta)^a], \quad (28)$$

with $z_c = -1$ and $a = 2$, we find that the closest singularity occurs at $\zeta = -2$. This means that the nonanalyticity at $z = -1$ takes the form $(1 + \sqrt{1+z})^{-b}$, where the exponent b depends on m and l (for $m = l = 1$, $b = 1$).

Applying an Euler transform to move the singularity at -1 to infinity (either with or without first applying the unfolding transformation), we find the expected nonanalyticity at $z = 11.6048$ for all functions $S_{mi}(z)$. Neville tables locate the singularity to an accuracy of better than four significant digits. Since the location of the nonanalyticity is easily calculated to high accuracy from Eq. (27), we can make biased estimates of the exponent which converge considerably faster than the unbiased estimates. A square-root branch point seems to exist for all S_{mi} , although convergence was slow for higher values of l . For the function $S_{11}(z)$, which is shown in Sec. IV to be of central importance, the convergence was excellent and far fewer coefficients would have been sufficient to give the analytic properties to a very high accuracy.

IV. PHYSICAL RESULTS

To obtain predictions of the thermodynamic behavior of the hard-sphere gas from the solution of Eq. (1), we begin by using the well-known relationship¹³ between the pressure and the value of ρ_2 at contact

$$\beta P / \rho = 1 + \frac{1}{2} \rho^{-1} \rho_2(\sigma^+). \quad (29)$$

From Eq. (19), it is seen that this reduces to

$$\beta P / \rho = \theta(z) = 1 + \frac{1}{2} [z / (1+z)] [1 + z S_{11}(z)] \quad (30)$$

and we need only analyze the function $S_{11}(z)$ in order to obtain an equation of state. Unfortunately, the presence of ρ in Eq. (30) prevents it from being a fundamental thermodynamic equation, which would provide all thermodynamic information immediately.¹⁴ There are essentially two ways of treating this difficulty. The first possibility is to demand that the product property be satisfied, i.e.,

$$\lim_{x_{12} \rightarrow \infty} \rho_2(x_{12}) = \rho^2, \quad (31)$$

which leads to

$$\rho = z/(1+z). \quad (32)$$

Although the product property is desirable, the use of Eq. (32) leads to inconsistent thermodynamics. On the other hand, if we allow the violation of the product property, we can obtain a consistent thermodynamic description of the system directly from Eq. (30).

Using the thermodynamic identity

$$\left. \frac{\partial P}{\partial z} \right|_{T,V} = \frac{\rho}{\beta z}, \quad (33)$$

we find that

$$\rho = z \theta^{-1}(z) \exp\left(\int \frac{1}{z} [\theta^{-1}(z) - 1] dz\right), \quad (34)$$

where the constant of integration has been determined by the condition

$$\lim_{z \rightarrow 0} (\rho/z) = 1 \quad (35)$$

(ideal gas limit). Equation (34) is particularly convenient for numerical evaluation, since the integrand can be expressed in the form of a series in z and the integral can be carried out explicitly. In fact, a virial expansion for βP in powers of ρ can be obtained directly from Eqs. (30) and (34) by carrying out all operations on the series themselves. The first three virial coefficients obtained are exactly correct, but the fourth is about a factor of 8 too large and the subsequent coefficients alternate in sign.

The most accurate numerical evaluation of Eqs. (30) and (34), however, is obtained by evaluating $\theta(z)$ and the integrand in Eq. (34) first and then performing the subsequent operations algebraically instead of as series operations. Since both $\theta(z)$ and the integrand in Eq. (34) are nonanalytic at $z_1 = 11.6048$, we first unfolded the series using Eq. (28) with $z_c = z_1$ and $a=2$ and then calculated near-diagonal Padé approximants to the unfolded series. For more than about 30 coefficients, the numerical results were unique and consistent to better than four significant digits.

Figure 1 shows a plot of $\beta P/\rho$ vs z . The nonanalyticity is seen to be quite weak [approximately $0.025 \times (1 - z/z_1)^{1/2}$] and has been shown on an expanded scale in the inset. It should be noted that the square-root singularities in the remaining functions, $S_{mi}(z)$, are about 10 to 20 times stronger.

In Fig. 2, we have normalized ρ to the density

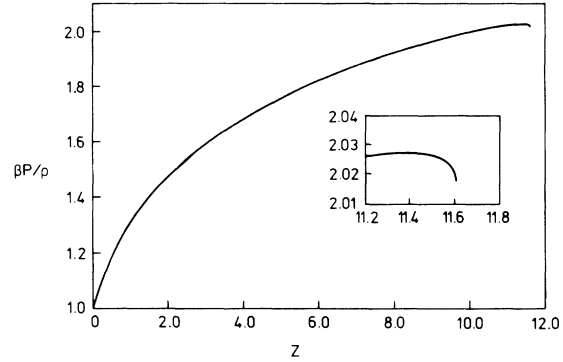


FIG. 1. $\beta P/\rho = PV/Nk_B T$ as a function of the activity z . The inset shows the square-root singularity at $z = 11.6048$ on an expanded scale.

at close packing, ρ_0 , and plotted ρ/ρ_0 vs z . We again see a square-root singularity, which is also shown on an expanded scale in the inset. Unfortunately, the value of ρ at the singularity is $\rho_1 = \rho(z_1) = 0.2716\rho_0$, which differs significantly from the Monte Carlo result of about $0.63\rho_0$.

Figure 3 shows $\beta P/\rho_0$ vs z , which is essentially the fundamental thermodynamic equation. The nonanalyticity takes the form of $(1 - z/z_1)^{3/2}$ and would not be visible even if the scale were to be expanded.

The equation of state, $\beta P/\rho_0$ vs ρ/ρ_0 , is shown in Fig. 4. P is an analytic function of ρ and the nonanalyticity in the fundamental equation is reflected only in the vanishing of the slope of this curve at ρ_1 (implying a divergence of the isothermal compressibility). The fact that $\partial P/\partial \rho = 0$ at ρ_1 is difficult to see from the direct plot in Fig. 4, so we have shown it again on an expanded scale in the inset. For comparison, Fig. 4 also shows a dashed line which plots a Padé-approximant equa-

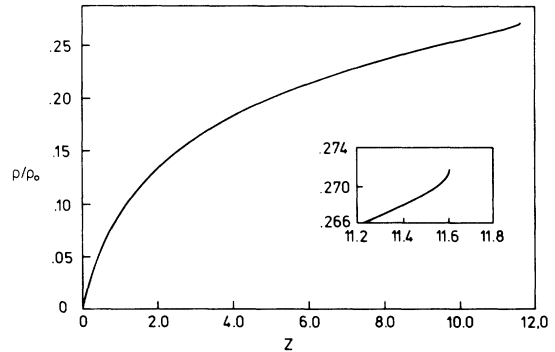


FIG. 2. ρ/ρ_0 as a function of the activity z (ρ_0 is the density at close packing). The inset shows the square-root singularity at $z = 11.6048$ on an expanded scale.

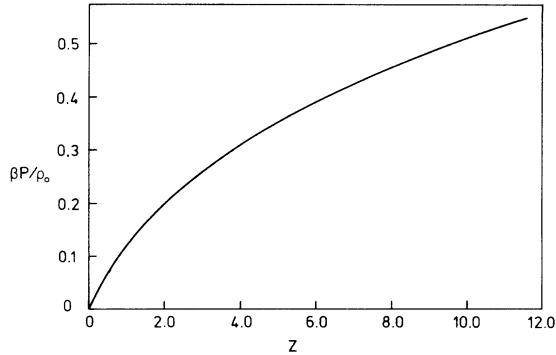


FIG. 3. $\beta P/\rho_0$ as a function of the activity z . This is essentially the fundamental thermodynamic equation of the system (ρ_0 is the density at close packing).

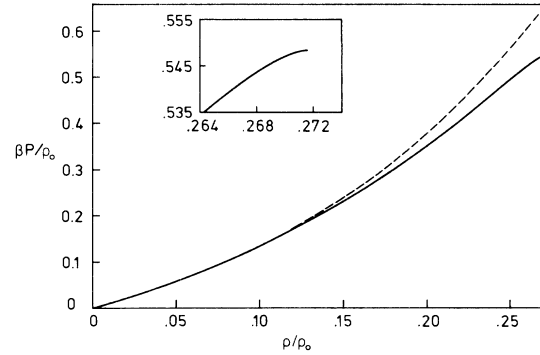


FIG. 4. Equation of state: $\beta P/\rho_0$ as a function of the density ρ/ρ_0 (ρ_0 is the density at close packing). The inset shows, on an expanded scale, the vanishing slope at $\rho = 0.2716\rho_0$.

tion of state proposed by Hall.¹⁵ This line provides an excellent fit to the Monte Carlo results of Adler and Wainwright.²

Since the divergence of the isothermal compressibility is characteristic of second-order phase transition (or perhaps a spinodal), we do not have a description of the first-order transition to the solid phase. On the other hand, the singularity in the fundamental equation has been shown to be very weak, so that, in some sense, we “almost” have a first-order transition. This result invites speculation on the possibility of an improved version of Eq. (1) actually describing a first-order phase transition. With this in mind, we would like to point out a property of Eq. (1) which might be relevant. Although Eq. (1) is only an approximation to the second Kirkwood-Salsburg equation, the exact equation can be written as

$$\rho_2(x_{12}) = R(x_{12}, \rho, z) + z(1 + f_{12}) \int \rho_2(x_{23}) f_{13} d^3x_{23}, \quad (36)$$

in which the inhomogeneous term contains integrals over higher-order correlation functions that are currently unknown. It is, of course, easy to imagine that the singularity we have found could be cancelled by a corresponding singularity in the inhomogeneous terms. However, it is perhaps not so obvious that the singularity in the fundamental equation can be eliminated [in the sense of $\rho_2(\sigma^+)$ being analytically continuable beyond the phase transition] without changing the analytic properties of the inhomogeneous term in the physical region. If the inhomogeneous term were to have the form

$$R(x_{12}, \rho, z) = z\rho(\sigma/x_{12})(1 + f_{12}), \quad (37)$$

the derivation given in Sec. II would only differ in the explicit form of the polynomial representation of P_1 . Carrying out the analysis of the new functions $S_m^R(z)$ in the manner described, we again find square-root singularities at $z = -1$ and $z = 11.6048$ for all functions S_m except S_{11} . To within the accuracy of the calculation (better than one part in 10^{30}) all expansion coefficients are those of the function

$$S_{11}^R(z) = (1 + \sqrt{1+z})^{-1}. \quad (38)$$

Since all thermodynamic properties are obtained from S_{11} , the equation of state would be analytically continuable through the phase transition with a nonzero isothermal compressibility, even though ρ_2 would not be analytically continuable as a function of z . This property is especially interesting in the light of a proof by Lanford and Ruelle¹⁶ that there exist correlation functions which are not analytically continuable through the first-order phase transition. The inhomogeneous term in Eq. (37) would be consistent with such a theorem and would still predict a complete absence of any precursor effect in any thermodynamic measurement. Unfortunately, it must be stressed that we have not derived Eq. (37) on physical grounds and the desirable properties of the solution given in Eq. (38) are only an indication of a possible form of a future theory.

ACKNOWLEDGMENTS

The authors would like to thank Professor M. S. Green for bringing this problem to their attention and for helpful and stimulating discussions. We would also like to thank Dr. Peter Kortman, and Dr. Norbert Grewe, and Professor David Landau for useful discussions.

- ¹For an overview, see H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, *Physics of Simple Fluids* (North-Holland, Amsterdam, 1968).
- ²B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* 33, 1439 (1960).
- ³J. G. Kirkwood and E. Monroe-Boggs, *J. Chem. Phys.* 10, 344 (1942).
- ⁴J. G. Kirkwood, E. K. Maun, and B. J. Alder, *J. Chem. Phys.* 18, 1040 (1950).
- ⁵M. S. Wertheim, *Phys. Rev. Lett.* 10, 321 (1963).
- ⁶E. Theile, *J. Chem. Phys.* 39, 494 (1963).
- ⁷M. S. Wertheim, *J. Math. Phys.* 5, 643 (1964).
- ⁸J. G. Kirkwood and Z. W. Salsburg, *Discuss. Faraday Soc.* 15, 23 (1953).
- ⁹A. A. Sabry, *Physica (Utr.)* 54, 60 (1971). Unfortunately, Sabry's solution is incorrect as a result of the erroneous assumption that all derivatives of his function $u(r)$ are continuous at $r=\sigma$ (see Ref. 10).
- ¹⁰W. Klein, *J. Math. Phys.* 14, 1049 (1973).
- ¹¹D. L. Hunter and G. A. Baker, Jr., *Phys. Rev. B* 7, 3346 (1973).
- ¹²W. Klein (unpublished).
- ¹³T. L. Hill, *Statistical Mechanics* (McGraw-Hill, London, 1956), p. 237.
- ¹⁴H. B. Callen, *Thermodynamics* (Wiley, New York, 1960), p. 100.
- ¹⁵K. R. Hall, *J. Chem. Phys.* 57, 2252 (1972).
- ¹⁶O. E. Lanford, III, and D. Ruelle, *Commun. Math. Phys.* 13, 194 (1969).