Universality of the cluster integrals of repulsive systems

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(Received 24 February 1987)

We provide evidence for the universal behavior of the exponent characterizing the singularity of the Mayer fugacity series for the pressure of a fluid. As long as the two-body potential is positive but otherwise unrestricted, this exponent appears to be independent of the form of the potential and it is a monotonic, slowly increasing function, $\phi(D)$, of the dimensionality D of the system. A limited version of universality has previously been proposed by Poland [J. Stat. Phys. **35**, 341 (1984)], restricted to hard, approximately spherical particles. Our results for $\phi(D)$ differ somewhat from those of Poland.

I. INTRODUCTION

It is well known that the radius of convergence R of the Mayer series expansions of the pressure $p(z)$ and number density $\rho(z)$ of a fluid phase in powers of the fugacity z is dramatically smaller than the fugacity z_1 associated with the transition to an ordered phase. The value of R is fixed by the presence of an algebraic singularity at the point $-R$ on the negative real z axis. The occurrence of this dominant singularity is a direct consequence of an extremely important theorem due to Groeneveld[1] applying to systems of particles interacting via a positive two-body potential. In practical terms, the singularity at $-R$ presents a major obstacle with regard to efforts to obtain estimates of z_1 and the corresponding critical exponent of the pressure. This is because an asymptotic analysis of the Mayer series can only provide the location of the singularity closest to the origin (the "dominant singularity") as well as the corresponding exponent, labeled ϕ in the following, characterizing the singular behavior of $p(z)$. There is an important exception to this pessimistic scenario.[2] If one had sufficiently accurate estimates of R and ϕ, one could employ a suitably chosen conformal mapping giving rise to a transformed series whose radius of convergence is determined by the physical singularity z_1. To achieve this, the point $-R$ must be mapped to the exterior of the new circle of convergence. As a first step in this direction, we will be concerned here with the determination of the exponent ϕ. In this article we provide numerical evidence for the *universality* of ϕ, depending solely on the dimensionality D of the system, for any lattice gas or any model of a fluid in continuous space based on an arbitrary although exclusively positive (see Sec. IV) two-body potential. Poland[3] has previously suggested that ϕ is universal for approximately spherical, hard particles. We will show here that Poland's twin restrictions [(i) hard-core interactions, (ii) approximately spherical particles] can both be waived. Moreover, our results for $\phi(D)$ differ somewhat from his.

To test the notation of universality for nonspherical particles we have obtained numerical estimates of $\phi(D)$ for the model of parallel hard hypercubes in continuous space.[4] Likewise, to study soft repulsive two-body interactions we have considered the Gaussian model,[5] whereby $f(r)=-\exp(-\tau r^2)$ is adopted for the Mayer function. The quantity $-k_B T\ln(1+f)$ is a short-ranged positive two-body effective potential diverging logarithmically for $r\to 0$ having the unphysical property of being temperature dependent. For both of these models cluster integrals (see below) can be obtained for arbitrary values of D, integer or otherwise. This enables us to study the dependence of ϕ on the continuous variable D.

A crucial test of the universality of ϕ can be made for two-dimensional systems. In the Appendix we derive the exact analytical result $\phi(2)=\frac{5}{6}$ for the hard hexagon model,[6–8] which is a triangular lattice gas with nearest-neighbor exclusions. For all the two-dimensional models we have considered our numerical results for ϕ (see Table I) are in fact consistent with this value, $\phi(2)=\frac{5}{6}$. On a considerably weaker footing, we offer some evidence suggesting that, as D increases, ϕ tends to $\phi(\infty)=\frac{3}{2}$. Furthermore, we remark that for all D our results are well described by the formula $\phi(D)=\frac{3}{2}-(\frac{2}{3})^{D-1}$. In particular, this simple analytic expression reproduces the exact values $\phi(0)=0$, $\phi(1)=\frac{1}{2}$, $\phi(2)=\frac{5}{6}$, which are presented in Sec. II. For $D=3$ this formula yields $\phi(3)=\frac{19}{18}=1.0555\ldots$ Our numerical estimates for a variety of three-dimensional systems (Table II) are consistent with this value. By contrast, Poland[3] has suggested that $\phi(1)=\frac{1}{2}$, $\phi(2)=\frac{4}{5}$, $\phi(3)=1$. His proposal for $D=2$ is in conflict with the exact result for the hard hexagon model. Furthermore, his proposal for $D=3$ is consistently smaller that all of our estimates in Table II.

To provide the necessary background material as well as to fix the notation we very briefly review some well-known facts. A complete description of the fluid phase is provided by the well-known Mayer series for the pressure

TABLE I. Estimated values of ϕ for two-dimensional systems. For the lattice gases nearest-neighbors, next-nearest-neighbors, and next-next-nearest-neighbor exclusions ($n=1,2,3$, respectively) are considered. M denotes the number of cluster integrals available.

Model	M	ϕ	Reference
Square lattice ($n=1$)	18	0.83(1)	30
Square lattice ($n=2$)	16	0.83(1)	31
Triangular lattice ($n=1$)	(exact)	0.8333. . .	Appendix
Triangular lattice ($n=2$)	10	0.83(1)	32
Triangular lattice ($n=3$)	9	0.83(1)	3
Square lattice, dimers	12	0.836(5)	33
Parallel hard squares	7	0.83(1)	4
Hard disks	7	0.82(2)	34
Gaussian	8	0.835(2)	5,20

in powers of the fugacity z,

$$\beta p = \sum_{n=1}^{\infty} b_n z^n \ . \tag{1}$$

Here $\beta = 1/(k_B T)$, k_B is Bolzmann's constant, T is the absolute temperature, and the coefficients $\{b_n\}$ are the Mayer cluster integrals. The number density follows from (1) as

$$\rho = z\frac{\partial}{\partial z}(\beta p) = \sum_{n=1}^{\infty} n b_n z^n \ . \tag{2}$$

In principle the equation of state of the fluid can be determined in terms of the cluster integrals upon eliminating z between (1) and (2). Each cluster integral is expressible in terms of irreducible integrals.[9] However, in practice the number of irreducible integrals contributing to b_n, for a given value of n, increases extremely rapidly with n. Moreover, their evaluation is generally notoriously complicated. Nevertheless, in the case of particles interacting via a positive two-body central potential, Groeneveld's theorem[1] provides a number of extremely important general statements concerning the cluster integrals as well as the radius of convergence of the infinite series in (1) and (2). First, b_n is positive (negative) for odd (even) n. This is the source of the fact that the dominant singularity of the series (1) and (2) is situated at a point $z=-R$ on the negative real axis and that R is the radius of convergence of the series. Second, $|b_n|$ satisfies the inequalities

$$1/n \le |b_n|/(2|b_2|)^{n-1} \le n^{n-2}/n! \ , \tag{3}$$

implying that R obeys the constraint $(2e|b_2|)^{-1} \le R \le (2|b_2|)^{-1}$. With $z=-R$ assumed to be an isolated algebraic singularity of $p(z)$ with exponent ϕ, the limiting behavior of $p(z)$ is described by[10,11]

$$\beta p \to C[(z+R)^{\phi} - 1]/\phi \quad (z \to -R) \ . \tag{4}$$

Invoking Darboux's theorem[12] it follows that the leading asymptotic behavior of b_n for large n is given by

$$b_n \sim (-1/R)^{n-1}[CR^{\phi}/\Gamma(\phi+1)]n^{-(\phi+1)} \ , \tag{5}$$

where the numerical value of ϕ must be determined for each separate model. We are claiming that ϕ is universal, and thus, if its value is known for a particular model the same value of ϕ applies for all other models (with exclusively positive two-body interactions) of the same spatial dimensionality.

We remark that in contrast to the universal behavior of ϕ associated with the singularity at $-R$, the exponent ϕ_1 corresponding to the physical singularity z_1 is definitely model dependent.[13,14] In fact, for some systems the accompanying transition is of first order, while for others it is of second order. Finally, it is appropriate to briefly justify the fact that our entire discussion relates to systems with exclusively positive two-body interactions. There is considerable evidence suggesting that the structure of a fluid as well as the nature of the fluid-solid transition is determined primarily by the short-range repulsive component of the two-body potential. The long-range attractive component is relatively weak, and as far as the structure of the fluid is concerned, can be treated as a perturbation.[15,16] As a result, a great deal of effort has been made in studying the equation of state and the properties of the melting transition for a variety of continuum fluid models as well as less realistic, yet mathematically simpler, lattice models based exclusively on repulsive two-body interactions.

In Sec. II we summarize the few cases where the exact value of ϕ is known. This enables us to test the idea of universality of ϕ, for if this idea is correct, all systems (with a positive two-body potential) of the same dimensionality must have the same value. In addition, knowledge of exact values of ϕ aids in the task of constructing the functional form of the universal function $\phi(D)$. Numerical results for ϕ are provided in Sec. III for an assortment of models. In Sec. IV we provide a discussion of our results and its potential implications for the problem of obtaining improved estimates of both the

TABLE II. Estimated values of ϕ for three-dimensional systems. M denotes the number of cluster integrals employed.

Model	M	ϕ	Reference
sc lattice	11	1.07(2)	6
bcc lattice	11	1.08(2)	6
sc lattice, dimers	12	1.08(1)	33
Parallel hard cubes	7	1.04(5)	4
Hard spheres	7	1.04(5)	35
Gaussian	8	1.09(1)	5,20

physical singularity z_1 and the corresponding critical exponent ϕ_1. Finally, in the Appendix we derive the value of ϕ for the hard hexagon model.

II. EXACT RESULTS

The exact values of ϕ can be calculated for a few specific models for the special dimensionalities $D=0,1,2$. We summarize these cases in this section.

The notation of a system in a zero-dimensional space can be realized by analytic continuation of results derived for $D>0$. One can show[17] that if $D=0$ the exact value of b_n is given by $b_n=(-1)^{n+1}/n$ for any model featuring a two-body potential which diverges to $+\infty$ for $r\to 0$. In particular, for this choice of D the quantity $|b_n|/(2|b_2|)^{n-1}$ assumes the lower bound, $1/n$, in the Groeneveld inequality (3). The radius of convergence of the Mayer series is given by $R=1$. It follows from (1) and (2) that for these systems

$$\beta p=\ln(1+z)\ , \tag{6}$$

$$\rho=z/(z+1)\ , \tag{7}$$

$$p=-k_B T\ln(1-\rho)\ . \tag{8}$$

Comparing either (6) with (4), or the present result for b_n with (5) yields $\phi(0)=0$, corresponding to $\rho,p\to-\infty$. The physical singularity of (6) occurs for $z\to\infty$, corresponding to $\rho=1,p\to\infty$.

For $D=1$ one can readily show that $\phi=\frac{1}{2}$ for lattice models featuring an arbitrary yet finite number of exclusions, as well as the continuum fluid of impenetrable lines. The simplest way to derive this result is to use Eq. (10) of Ref. 18, giving z as a function of p, so as to show that $p(z)\to p(-R)+C(z+R)^{1/2}$ for $z\to -R$.

The hard hexagon model[6] is unique in that an exact solution applicable for all densities has been obtained by Baxter.[7,8] In particular he derived a parametric representation of the fugacity and the grand partition function per lattice site of an infinite lattice κ and showed that there exists a singularity on the positive real z axis at the point $z_1=(2\cos\pi/5)^5=(11+5\sqrt{5})/2=11.090\,17\ldots$, and the corresponding exponent of the pressure series is $\phi_1=\frac{5}{3}$. This singularity is associated with a second-order transition from a homogeneous fluid phase to an ordered inhomogeneous phase. By contrast, the singularity of κ determining the radius of convergence of the Mayer series is situated[19] on the negative real-z axis at the point $z=-R$, where $R=1/z_1=(5\sqrt{5}-11)/2=0.090\,169\,94\ldots$. Starting from Baxter's parametric representation of κ and z and using standard properties of theta functions we find that the leading nonanalytic term contributing to $p(z)$ for $(z+R)\to 0$ is of the form $(z+R)^{5/6}$, so that $\phi=\frac{5}{6}$. The details of the derivation are given in the Appendix.

III. NUMERICAL RESULTS

In contrast to the solvable models described in the previous section, for the remaining continuous space and lattice models of a fluid considered in the literature, our information concerning the equation of state consists of the first M cluster integrals b_n. For the various lattice models typically 10 to 20 cluster integrals are known, whereas $M\le 7$ for the continuum models, with the exception of the Gaussian model for which b_8 has been derived recently by one[20] of us. Estimates for the location of the singularity of the Mayer series on the negative real-z axis and its corresponding critical exponent ϕ can be obtained by applying standard[21] numerical methods to the known cluster integrals. In particular, we have applied the ratio method to the series (1) and (2) as well as to the quantity $z\partial\rho/\partial z$ for a variety of lattice gas and continuous space models. We have also utilized the methods of Padé and Levin approximants[22–24] for these models.

In Table I we list our best estimates of ϕ for various two-dimensional systems, mostly lattice gas models as well as three continuum models, specifically the system of hard disks, parallel hard squares, and the Gaussian model. The quantity M in Tables I and II is the number of cluster integrals used. For each listed value of ϕ we have included our estimate of the uncertainty of the last digit and this is enclosed in parentheses. In the case of the hard disk system our estimate also reflects the current uncertainties in the values of b_6 and b_7. Note that the interaction potential ranges from spherically symmetric (hard disks, Gaussian model) to highly anisotropic (dimers). Nevertheless, in all cases the results are consistent with the exact value $\phi(2)=\frac{5}{6}=0.8333\ldots$ for the hard hexagon model. Furthermore, as stated earlier, this value is somewhat larger than Poland's[3] proposal, $\phi(2)=\frac{4}{5}$.

In Table II we list our estimates for ϕ for various three-dimensional models. As for the two-dimensional systems, it appears that ϕ is independent of the details of the potential and depends only upon the dimensionality of the system. As remarked in the Introduction, the function $\phi(D)=\frac{3}{2}-(\frac{2}{3})^{D-1}$ correctly reproduces the exact values of ϕ for $D=0,1,2$ whereas for $D=3$ it gives the value $\frac{19}{18}=1.0555\ldots$, which is generally consistent with the data in Table II. In any event, all of our numerical estimates for ϕ in Table II are consistently larger than Poland's proposed value $\phi(3)=1$.

Finally, in Table III we provide estimates for ϕ in the range $0\le D\le 6$ for both the Gaussian[5] and the parallel[4] hard hypercubes (PHH) models. For the smaller values of D the estimates for the two models are in good agreement, whereas there is a steadily increasing deviation between the estimates as D increases. We cannot rule out the possibility that this is evidence for the lack of universality. A more likely explanation, however, is that for increasingly larger D our estimates for ϕ are simply unreliable, for the following reason. Standard Darboux analysis[21] of (4) shows that a rigorous value of $\phi(D)$ is given by $\lim\phi_n(D)$, where

$$\phi_n(D)\equiv -1+n\,[1-R(D)\,|b_n(D)|\,/\,|b_{n-1}(D)|\,]\ ,$$

and the limit is taken for $n\to\infty$ while D is held fixed. We are, of course, at present limited to values of b_n for $n\le 8$ in the case of the Gaussian model and $n\le 7$ for the PHH model. As D is increased while n is held fixed the behavior of b_n will very rapidly become dominated[25] by the contribution of the Cayley tree diagram, i.e.,

TABLE III. Estimated values of ϕ for the Gaussian model and the model of parallel hard hypercubes as a function of dimensionality D.

D	Gaussian	Hypercubes
0	0	0
0.25	0.1491(1)	0.150(2)
0.50	0.279(1)	0.283(4)
0.75	0.396(1)	0.396(1)
1.00	0.500(1)	0.500(1)
1.25	0.595(1)	0.592(1)
1.50	0.680(2)	0.676(3)
1.75	0.760(3)	0.755(5)
2.00	0.835(2)	0.830(10)
2.25	0.905(2)	0.888(4)
2.50	0.969(2)	0.950(10)
2.75	1.029(2)	1.000(10)
3.00	1.086(3)	1.045(10)
3.50	1.180(5)	1.122(5)
4.00	1.269(5)	1.200(20)
4.50	1.332(2)	1.260(30)
5.00	1.381(1)	1.300(50)
5.50	1.418(1)	1.350(60)
6.00	1.444(1)	1.410(60)

$b_n \sim (-2b_2)^{n-1}n^{n-2}/n!$. Therefore, if we use the values of $\phi_n(D), n \leq 8$ to estimate $\phi(D)$ for larger D the resulting values can be expected to be misleading, i.e., excessively dominated by the Cayley tree diagram. Note, however, that for $D=4$ the analytic expression $\phi(D)=\frac{3}{2}-(\frac{2}{3})^{D-1}$ suggested above equals 1.2037. . . which is consistent with our estimate for the PHH model.

It is of interest to consider the question of the value of $\phi(\infty)$. As D is increased from zero the value of $|b_n|/(2|b_2|)^{n-1}$, for fixed n, increases from $1/n$ towards $n^{n-2}/n!$. These are the greatest lower bound and least upper bound in the Groeneveld inequalities (3). We conjecture that in the limit $D\rightarrow\infty$ the Cayley tree approximation is strictly valid and in particular that $\phi(\infty)=\frac{3}{2}$. A proper proof of this conjecture is, however, required. Using the exact formal expression for ϕ given in the previous paragraph it is clear that calculation of $\phi(\infty)$ requires taking the limit $n\rightarrow\infty$ *followed* by the limit $D\rightarrow\infty$. If reversal of the order of the limits were justifiable then the result would be $\phi=\frac{3}{2}$. In the absence of any information concerning the large-n behavior of $b_n(D)$ for fixed D we are of course unable to justify such a reversal.

IV. DISCUSSION

In this work we have provided numerical evidence for the universal character of the critical exponent ϕ associated with the dominant mathematical singularity of the Mayer series, for a fluid with positive two-body interactions. The value of ϕ depends solely on the spatial dimensionality of the system and $\phi(D)$ is a monotonic increasing function of D ranging from unity for $D=0$ to $\frac{3}{2}$ for $D\rightarrow\infty$. The simple analytic expression $\phi(D)=\frac{3}{2}-(\frac{2}{3})^{D-1}$ correctly reproduces the known exact values of ϕ for $D=0,1,2$, and it provides results in close agreement with our numerical estimates for other values of D. Furthermore, our data for ϕ suggests that universality occurs for any, exclusively positive, two-body potential. In particular, we find that there is no justification for Poland's[2] restriction of universality to hard, approximately spherical particles.

It is important to note that the universal behavior of ϕ breaks down if the restriction to an exclusively positive two-body interaction is relaxed. We have shown this explicitly for a lattice gas model due to Fisher,[26] describing particles on a square lattice with nearest-neighbor exclusions and weak second-neighbor attractions between selected lattice sites. We have found[27] that for this model the limiting form of $p(z)$ for $z\rightarrow -R=(1-\sqrt{2})/2$ is $p(z)\rightarrow(z+R)\ln(z+R)$ so that $\phi=1$. We attribute this deviation of ϕ from the value $\phi(2)=\frac{5}{6}$ to the presence of the attractive interactions incorporated in the model.

Ultimately, the primary practical significance of the universal behavior of ϕ is its potential utility in eliminating the debilitating effects of the small radius of convergence of the Mayer series. A judiciously conceived conformal mapping, embodying sufficiently accurate estimates of R and ϕ should aid in suppressing the effects of this spurious singularity. The radius of convergence of the resulting transformed series would then be determined by the physical singularity, as long as under the mapping the singularity of the Mayer series is transformed to the exterior of the new circle of convergence. One can use standard methods of series analysis[21] to exploit an accurate estimate (or exact value) of ϕ so as to improve estimates of R. We are currently pursuing such a study of several models of fluids and our results will be reported elsewhere.

Note added in proof. A. J. Guttmann [J. Phys. A **20**, 512 (1987)] has very recently obtained the numerical estimate $\phi=0.833\,37$ for the hard square lattice gas and he conjectures that $\phi=\frac{5}{6}$ is the exact value. This provides important additional evidence supporting our claim of the universal behavior of ϕ.

ACKNOWLEDGMENTS

It is a pleasure to thank S. Baer of the Hebrew University of Jerusalem, Israel for several helpful discussions and James H. Luscombe of the Ames Laboratory for helpful suggestions concerning the manuscript. The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This work was supported by the Office of Basic Energy Sciences.

APPENDIX

In this appendix we derive the value of the exponent ϕ associated with the singularity of the Mayer series for the hard hexagon model. Baxter[7] has shown that the fugacity z and the grand partition function per lattice site, $\kappa=Z^{1/N}$, can be expressed in terms of a variable x, with $|x|<1$, according to the formulas

$$z=-xg^5(x),\quad \kappa(x)=g^2(x)g_1(x)h_0(x)h_1(x)\,, \tag{A1}$$

where

$$g(x)=\prod_{n=1}^{\infty}\frac{(1-x^{5n-4})(1-x^{5n-1})}{(1-x^{5n-3})(1-x^{5n-2})}\,, \tag{A2a}$$

$$g_1(x)=\prod_{n=1}^{\infty}\frac{(1-x^{5n})^2}{(1-x^{5n-3})(1-x^{5n-2})}\,, \tag{A2b}$$

$$h_0(x)=\prod_{n=1}^{\infty}\frac{(1-x^{6n-3})}{(1-x^{6n-1})(1-x^{6n-5})}\,, \tag{A2c}$$

$$h_1(x)=\prod_{n=1}^{\infty}\frac{(1-x^{6n-4})(1-x^{6n-2})}{(1-x^{6n})^2}\,. \tag{A2d}$$

Each of these functions is analytic in x for $|x|<1$ and the circle $|x|=1$ is a natural boundary. As we shall presently show, the singularity of the Mayer series occurs for $z=-R=-(5\sqrt{5}-11)/2$, corresponding to the point $x=1$. We can derive the value of ϕ by establishing the dependence of the pressure $p=k_BT\ln\kappa$ on the variable z in the immediate vicinity of $z=-R$ and comparing with (4). This will be achieved by eliminating x between z and κ. The required calculations become straightforward when we exploit the formula derived by Baer[28] which express the functions in (A2) in terms of theta functions. The dominant behavior of these functions for $x\to 1-$ is established upon using what is known as the Jacobi imaginary transformation.

Defining a quantity σ by $x=\exp(i\pi\sigma)$, Baer[28] has shown that

$$g(x)=\Theta_4(3\pi\sigma/4\mid 5\sigma/2)/\Theta_4(\pi\sigma/4\mid 5\sigma/2)\,, \tag{A3a}$$

$$g_1(x)=\tfrac{1}{2}[\Theta_1'(0\mid 5\sigma/2)/\Theta_4(\pi\sigma/4\mid 5\sigma/2)]\times\exp(-5\pi\sigma i/8)\,, \tag{A3b}$$

$$h_0(x)=\Theta_4(0\mid 3\sigma)/\Theta_4(\pi\sigma\mid 3\sigma)\,, \tag{A3c}$$

$$h_1(x)=2[\Theta_4(\pi\sigma/2\mid 3\sigma)/\Theta_1'(0\mid 3\sigma)]\exp(3\pi\sigma i/4)\,. \tag{A3d}$$

The quantities Θ_1 and Θ_4 appearing in these equations are Θ functions. We employ the notation and properties of these functions as given in Chap. 21 of Whittaker and Watson.[29] (As a word of caution, Baer[28] utilizes a different notation.) We also note the identity (p. 470 of Ref. 29)

$$\Theta_1'(0\mid\tau)=\Theta_2(0\mid\tau)\Theta_3(0\mid\tau)\Theta_4(0\mid\tau)\,. \tag{A4}$$

To investigate the behavior of the functions in (A3) and (A4) for real values of x in the limit $x\to 1-$, we set $\sigma=i\epsilon/\pi$ where ϵ is a small real positive number so that $x=e^{-\epsilon}$. The limiting form of each of these functions for $\epsilon\to 0+$ is easily obtained by exploiting Jacobi's imaginary transformations (pp. 474–476 of Ref. 29),

$$\Theta_2(0\mid\tau)=(-i\tau)^{-1/2}\Theta_4(0,e^{-i\pi/\tau})\,, \tag{A5a}$$

$$\Theta_3(0\mid\tau)=(-i\tau)^{-1/2}\Theta_3(0,e^{-i\pi/\tau})\,, \tag{A5b}$$

$$\Theta_4(z\mid\tau)=(-i\tau)^{-1/2}\exp[-iz^2/(\pi\tau)]\Theta_2(-z/\tau,e^{-i\pi/\tau})\,. \tag{A5c}$$

For each of the theta functions in (A3) the value of the second variable is of the form $\tau=c_2\sigma=ic_2\epsilon/\pi$, where c_2 is a real positive number. It therefore follows that $e^{-i\pi/\tau}=\exp[-\pi^2/(c_2\epsilon)]$ is an extremely small real positive number. We may therefore approximate the series expansions (p. 464 of Ref. 29) of the theta functions on the right-hand side of (A5) as

$$\Theta_2(y,q)\simeq 2q^{1/4}[\cos y+q^2\cos(3y)+O(q^6)]\,,$$

$$\Theta_3(0,q)\simeq 1+2q+O(q^4)\,,$$

$$\Theta_4(0,q)\simeq 1-2q+O(q^4)\,.$$

One thereby obtains the following limiting expressions for $x\to 1-$:

$$g(x)\to\tfrac{1}{2}(\sqrt{5}-1)e^{\epsilon/5}(1-\sqrt{5}e^{-4\pi^2/(5\epsilon)}+\cdots)\,, \tag{A6a}$$

$$g_1(x)\to\frac{\pi e^{3\epsilon/5}}{5\epsilon\cos(\pi/10)}[1-e^{-4\pi^2/(5\epsilon)}\sqrt{5}(\sqrt{5}+1)]\,, \tag{A6b}$$

$$h_0(x)\to 2(1+3e^{-2\pi^2/(3\epsilon)})e^{-\epsilon/3}\,, \tag{A6c}$$

$$h_1(x)\to(3^{3/2}/\pi)\epsilon e^{-2\epsilon/3}(1+3e^{-2\pi^2/(3\epsilon)})\,. \tag{A6d}$$

In the process of obtaining some of these formulas we used the trigonometric formula for the golden mean, $2\cos(\pi/5)=(\sqrt{5}+1)/2$. Substitution in (A1) leads directly to the following limiting behavior of z as $\epsilon\to 0+$ ($x\to 1-$):

$$z(x)\to -R(1-5\sqrt{5}e^{-4\pi^2/(5\epsilon)})\,, \tag{A7}$$

where $R=(5\sqrt{5}-11)/2$, and we recall that $x=e^{-\epsilon}$. Likewise, we obtain the following limiting form of κ:

$$\kappa(x)\to\kappa_0(1+6e^{-2\pi^2/(3\epsilon)})\,, \tag{A8}$$

where

$$\kappa_0=3\sqrt{3}(\sqrt{5}-1)^2/[10\cos(\pi/10)]\,. \tag{A9}$$

Eliminating ϵ between (A7) and (A8) yields

$$\kappa(z)\to\kappa_0\{1+6\times 5^{-5/4}[(z/R)+1]^{5/6}\}\,. \tag{A10}$$

Finally, the pressure is given by

$$\beta p(z)=\ln\kappa_0+6\times 5^{-5/4}[(z/R)+1]^{5/6}\,. \tag{A11}$$

In particular, if we compare (A11) with (4) we have the claimed result $\phi=\frac{5}{6}$. In closing, we remark that this derivation shows that $z=-R$ is indeed a singularity of $p(z)$ on the negative real-z axis. Consider the narrow strip $|\mathrm{Im}x|<\eta$, where $\eta\ll 1$, with $-1<\mathrm{Re}x<1$. Within this strip the functions $z(x)$ and $\kappa(x)$ are analytic functions of x. Furthermore, one can show that $z'(x)$ is nonzero within this strip. It therefore follows that κ is an analytic function of z in the immediate vicinity of the real z axis between $-R$ and z_1. We may therefore legitimately identify R with the radius of convergence of the Mayer series.

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[10]Note that the isothermal compressibility K_T can be written as $K_T=(\beta/\rho^2)\chi(z)$, where $\chi(z)=z\partial\rho/\partial z\propto(z+R)^{-(2-\phi)}$ for $z\rightarrow R$.

[11]The form chosen in (4) enables us to include the case where $\phi\rightarrow 0$, which as shown in Sec. II occurs for $D=0$, so that $\beta p\rightarrow C\ln(z+R)$.

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[14]At least two different scenarios are possible with regards to the meaning of z_1. For some lattice gas models the fluid gives way to an ordered phase with an accompanying second-order transition at the density ρ_1. In a second scenario, the fluid undergoes a first-order transition to another phase for a density, ρ_c, where $\rho_c<\rho_1$. For densities between ρ_c and ρ_1 the Mayer series presumably describes a metastable fluid phase. We anticipate that the pressure of that phase increases monotonically and diverges as z is increased towards the singularity at z_1. We have suggested that this occurs in dense systems of hard spheres or hard disks (see Ref. 23).

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