Journal of Statistical Physics, Vol. 35, Nos. 3/4, 1984

On the Universality of the Nonphase Transition Singularity in Hard-Particle Systems

Douglas Poland[1]

Received August 15, 1983; revision received November 29, 1983.

Activity series for hard-particle lattice gases and hard particles in continuous space are examined with respect to the singularity on the negative activity axis. For approximately spherical particles it is found that the nature of the singularity depends only on the dimensionality of space.

KEY WORDS: Hard particles; activity series; radius of convergence; singularities; exponents.

1. INTRODUCTION

For hard-particle systems such as a gas of hard spheres, the coefficients b_n in the Mayer activity series for the pressure

$$\beta p = \sum_n b_n z^n \tag{1.1}$$

(where p is the pressure, $\beta = 1/kT$, and z is the activity) are known[1] to alternate in sign and hence point to a singularity on the negative z axis that determines the radius of convergence of the series. Rigorous upper and lower bounds for the radius of convergence of activity series for hard-particle systems are known.[2] From the study of activity series for lattice gases with repulsive interactions only,[3,4] the position of the singularity on the negative z axis, which we will refer to as $z_\sigma^{(-)}$, has been determined for a number of systems; in general $z_\sigma^{(-)}$ is very close to the origin and this singularity completely dominates the behavior of the activity series. Because of the presence of this dominant nonphysical singularity (not associated with a phase transition) it is very difficult to use activity series for

[1] Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218.

0022-4715/84/0500-0341$03.50/0

hard-particle systems to locate singularities on the real positive z axis that are associated with phase transitions.

A good example is the lattice gas on the quadratic lattice with nearest-neighbor exclusion. Gaunt and Fisher[3] found a singularity in Eq. (1.1) for this system at

$$z_\sigma^{(-)} = -0.119 \tag{1.2}$$

From the study of other thermodynamic functions (particularly, high-density series) an additional singularity has been located[3,5] on the positive z axis at

$$z_\sigma^{(+)} = 3.76 \tag{1.3}$$

The singularity at $z_\sigma^{(+)}$ is of interest since it is associated with the sublattice order–disorder transition found in this system. On forming the ratio of the numbers in (1.2) and (1.3),

$$|z_\sigma^{(+)}|/|z_\sigma^{(-)}| = 32$$

one sees that the singularity on the negative axis is 32 times closer to the origin than the phase-transition singularity on the positive axis.

Because of the dominance of $z_\sigma^{(-)}$ in hard-particle systems, we have surveyed the nature of this singularity for a variety of lattice-gas models and hard-particle systems in continuous space (hard disks and hard spheres). If z is expressed in natural units (measuring the volume relative to the volume per particle at close packing), then we find striking similarities in the values of $z_\sigma^{(-)}$ and the exponent associated with this singularity. In particular, we find that the exponent depends on the dimensions of space only (for approximately spherical particles). This is in contrast to the nature of the phase-transition singularity, the transition being second order for some lattice gases,[3–6] first order for others,[6] and first order for disks and spheres.[7]

We begin our survey by examining hard-particle systems in two dimensions that exhibit hexagonal packing in the high-density limit.

2. TWO-DIMENSIONAL SYSTEMS WITH HEXAGONAL PACKING

Figure 1A illustrates several different lattice gases on the triangular lattice that give a hexagonal array of particles in the close-packing limit. In each the central solid circle marks the location of the particle; the surrounding solid circles mark sites that are excluded from occupany by other particles. Following Nisbet and Farquhar,[6] we use the labels TR1 and TR12 to refer to the models, respectively, where the first hexagon of sites surrounding a particle (nearest-neighbor exclusion), and the first and second hexagons of sites surrounding a particle cannot be occupied by another particle. The b_n for TR1 are known as a by-product of the series for the

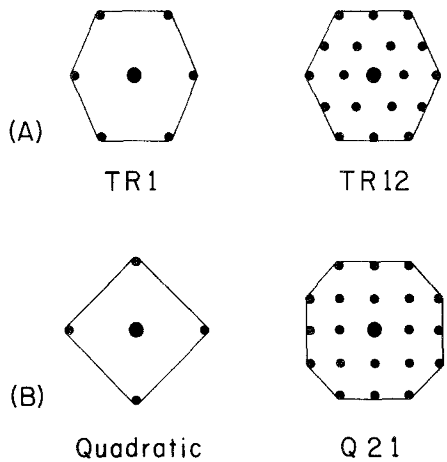

Fig. 1. (A) Lattice gases based on the triangular lattice. (B) Lattice gases based on the quadratic lattice. In each the solid circles indicate the lattice sites that are excluded from occupancy when a particle occupies the central site.

two-dimensional (2-d) Ising model on the triangular lattice[8] and have been studied by Gaunt.[4] Orban and Bellemans[9] give the activity series for TR12 through b_7 (TR1 and TR12 are models A and C of these authors). We have calculated b_8 and b_9 for TR12 using the Toeplitz matrix technique of Springgate and Poland[10]; the b_n through b_9 for TR12 are given in Table III. The set of models TR1, TR12, and hard disks can be viewed as a progression whereby the divisions of the triangular lattice grid are made finer, disks of course representing the continuous space limit (all three models exhibit hexagonal close packing, the reason they were chosen).

For hard disks in two dimensions the first four B_n are known exactly[11] and in addition the coefficients B_5 through B_7 have been calculated using Monte Carlo techniques.[12] These results are shown below (where σ is the diameter of the disk):

$$\begin{aligned}
B_1 &= 1 \\
B_2 &= (\pi/2)\sigma^2 \\
B_3 &= B_2^2\left(4/3 - \sqrt{3}/\pi\right) = B_2^2(0.7820044) \\
B_4 &= B_2^3\left(2 - 9\sqrt{3}/2\pi + 10/\pi^2\right) = B_2^3(0.5322318) \qquad (2.1) \\
B_5 &= B_2^4(0.3335561) \\
B_6 &= B_2^5(0.19893) \\
B_7 &= B_2^6(0.1148)
\end{aligned}$$

To convert the coefficients in the density expansion for the pressure, the B_n, to coefficients in the activity expansion, the b_n, one can use the standard relation

$$z = \rho \exp\left[\sum_{n=1}^{\infty} \left(\frac{n+1}{n} \right) B_{n+1} \rho^n \right] \tag{2.2}$$

which can be expanded to give a series for z as a function of ρ, the density. Inversion of the series yields

$$\rho = \sum_n n b_n z^n \tag{2.3}$$

giving the b_n.

To compare the series for various models it is convenient to scale ρ and z so as to make $\rho = 1$ at close packing. Letting v_0 be the volume (or area in two dimensions) per particle at close packing then the relative density and activity are

$$\begin{aligned} \bar{z} &= z/\rho_0 \\ \bar{\rho} &= \rho/\rho_0 \end{aligned} \tag{2.4}$$

where

$$\rho_0 = 1/v_0 \tag{2.5}$$

For lattice gases v_0 is the number of lattice sites per particle at close packing. For the models treated here (giving v_0 in parentheses) one has: TR1(3), TR12(7), and disks ($\sqrt{3}/2$); for disks we take the parameter, σ, as unity. The values of v_0 for all the models we will discuss are listed in Table I.

Scaling the b_n as follows,

$$\bar{b}_n = b_n / v_0^{\,n-1} \tag{2.6}$$

Table I. The Volume or Number of Lattice Sites, v_0, per Particle at Close Packing

Model	v_0
TR1 (2-d)	3
TR12 (2-d)	7
Quadratic (2-d)	2
Q21 (2-d)	8
sc (3-d)	2
fcc (3-d)	6
Quartic (4-d)	2
Disks (2-d)	$\sqrt{3}/2$
Spheres (3-d)	$1/\sqrt{2}$
Hyperspheres (4-d)	$1/2$

(1.1) becomes

$$\beta\bar{p}/\bar{z} = \beta p/z = 1 + \sum_{n=2}^{\infty} \bar{b}_n \bar{z}^{n-1} \tag{2.7}$$

The virial expansion for the pressure

$$\beta p = \sum_n B_n \rho^n \tag{2.8}$$

when expressed as a series in $\bar{\rho}$ becomes

$$\beta\bar{p}/\bar{\rho} = \beta p/\rho = 1 + \sum_{n=2}^{\infty} \bar{B}_n \bar{\rho}^{n-1} \tag{2.9}$$

where

$$\bar{B}_n = B_n / v_0^{\,n-1} \tag{2.10}$$

We have written (2.7) and (2.9) in the form given to emphasize the fact that

$$\begin{aligned} \bar{b}_1 &= b_1 = 1 \\ \bar{B} &= B_1 = 1 \end{aligned} \tag{2.11}$$

The density as a function of the activity is obtained in the standard manner

$$\bar{\rho} = \partial \beta p / \partial \ln \bar{z} \tag{2.12}$$

or

$$\bar{\rho} = \sum_n n \bar{b}_n \bar{z}^n \tag{2.13}$$

The values of $\bar{B}_n$ and $\bar{b}_n$ for disks are given in Table II.

The function we have chosen to study is the reduced compressibility[2]

$$\chi(\bar{z}) = \sum_n n^2 \bar{b}_n \bar{z}^n \sim \left(\frac{1}{\bar{z} - z_\sigma^{(-)}} \right)^{\nu} \tag{2.14}$$

which one expects to diverge strongly at $\bar{z}_\sigma^{(-)}$. Table IV shows the values of $\bar{z}_\sigma^{(-)}$ and ν for the models studied, obtained as denominator roots and their respective residues for the off-diagonal and diagonal Padé approximants to $D \log \chi$. The number of terms used in each case is indicated in Table IV.

As one goes from TR1 to TR12 to disks, one sees that $\bar{z}_\sigma^{(-)}$ moves slightly closer to the origin, but not by much. The important result is that the exponent ν is essentially the same for all three models. Specifically we find

$$\nu = 1.195 \pm 0.005 \tag{2.15}$$

[2] χ is related to the isothermal compressibility K_T by the relation $K_T = \beta\chi/\rho^2$; χ is the interesting (singular) part of K_T.

Table II. The Scaled Coefficients $\bar{B}_n$ and $\bar{b}_n$ for Hard Particles in Continuous Space

n	$\bar{B}_n$ Disks (2-d)	$\bar{B}_n$ Spheres (3-d)	$\bar{B}_n$ Hyperspheres (4-d)
1	1.000	1.000	1.000
2	1.814	2.962	4.935
3	2.573	5.483	12.33
4	3.176	7.456	18.19
5	3.610	8.486	
6	4.905	8.868	
7	4.088	9.250	
n	$\bar{b}_n$ Disks (2-d)	$\bar{b}_n$ Spheres (3-d)	$\bar{b}_n$ Hyperspheres (4-d)
1	1.000	1.000	1.000
2	− 1.814	− 2.962	− 4.935
3	5.293	14.80	42.54
4	− 18.88	− 92.35	− 464.4
5	75.33	651.8	
6	− 322.75	− 4978.3	
7	1452.9	40169.4	

[a] For simplicity we show only four to five figures.

where the ± indicates the approximate range of values found. Clearly it is possible that $\nu_{2\text{-d}} = 6/5$ exactly.

Thus all three models have the same kind of singularity at $\bar{z}_\sigma^{(-)}$. As mentioned in the Introduction this is in contrast to the behavior of the phase transition singularity at $\bar{z}_\sigma^{(+)}$: TR1 has a second-order transition, while TR12 and hard disks[6,7] have a first-order transition.

3. OTHER TWO-DIMENSIONAL LATTICE GASES

We have examined two other lattice gas models in two dimensions to test the notion that the singularity at $z_\sigma^{(-)}$ is the same for all 2-d hard-particle systems. The first of these models is the case of nearest-neighbor exclusion on the quadratic lattice [the model discussed in the Introduction in conjunction with Eq. (1.2) and (1.3)]. The b_n are known[8] for this system through $n = 15$ and thus give us a long, exact series with which to test the universality idea. (This system has been examined previously by Gaunt and Fisher[3] using the b_n through $n = 13$.) Again examining $D \log \chi$, one finds the results given in Table IV (listed under quadratic model).

The other model we examine, which we will call Q21, excludes 21 sites on the quadratic lattice, as illustrated in Fig. 1B. We have calculated the b_n

Table III. The b_n for Several Lattice Gases

n	TR12 (2-d)	Q21 (2-d)	Quartic (4-d)
1	1	1	1
2	$-9\frac{1}{2}$	$-12\frac{1}{2}$	$-16\frac{1}{2}$
3	$144\frac{1}{3}$	$252\frac{1}{3}$	$472\frac{1}{3}$
4	$-2675\frac{3}{4}$	$-6231\frac{1}{4}$	$-17{,}086\frac{1}{4}$
5	$55{,}426\frac{1}{5}$	$172{,}105\frac{1}{5}$	
6	$-1{,}232{,}512\frac{1}{6}$	$-5{,}105{,}377\frac{1}{6}$	
7	$28{,}792{,}636\frac{1}{7}$	$159{,}144{,}839\frac{1}{7}$	
8	$-697{,}475{,}676\frac{7}{8}$	$-5{,}145{,}013{,}626\frac{5}{8}$	
9	$17{,}372{,}452{,}613\frac{1}{9}$		

for this system through $n = 8$ (again using the Toeplitz matrix technique of Poland and Springgate[5]); these coefficients are given in Table III. The results of calculating the roots and residues of $D \log \chi$ are shown in Table IV.

Clearly the values of ν for both of these very different models are squarely in the range given by (2.15) and hence support the idea that the nature of this singularity is the same for all 2-d hard-particle models (for systems of approximately circular particles).

4. THREE-DIMENSIONAL MODELS

We have examined three models in three dimensions, hard spheres and two lattice-gas models[4,8] [particles with nearest-neighbor exclusion on the simple cubic (sc) and face-centered cubic (fcc) lattices]. The B_N for spheres, shown below, are known exactly through B_4[13] and have been calculated by Monte Carlo methods for B_5 through B_7.[14] The quantity σ is the diameter of the sphere:

$$\begin{aligned}
B_1 &= 1 \\
B_2 &= (2\pi/3)\sigma^3 \\
B_3 &= B_2^2(5/8) \\
B_4 &= B_2^3(0.28695) \qquad (4.1)\\
B_5 &= B_2^4(0.110252) \\
B_6 &= B_2^5(0.0389) \\
B_7 &= B_2^6(0.0137)
\end{aligned}$$

The scaled coefficients [using (2.6) and (2.10)] $\bar{B}_n$ and $\bar{b}_n$ are shown in Table II.

Examining $D \log \chi$ for all three models yields the results shown in Table IV. The values of $\bar{z}_\sigma^{(-)}$ are of the same order of magnitude for all three models. For spheres and the sc lattice gas (where we have 11 terms) the values of ν obtained are in the range

$$\nu = 1.01 \pm 0.01 \tag{4.2}$$

with the values of ν for the fcc lattice gas (where we have only six terms) being only slightly larger. Again, the values of ν are almost exactly the same for all the three-dimensional (3-d) models treated (the value of ν for the 3-d models being different from that for the 2-d models).

We can speculate that $\nu_{3\text{-d}} = 1$ exactly.

5. FOUR-DIMENSIONAL MODELS

We have found that $\nu_{2\text{-d}} \cong 6/5$ and $\nu_{3\text{-d}} \cong 1$. The question thus arises as to the values of ν for systems in higher dimensions. The first three B_n are known[15] exactly for hyperspheres in four dimensions and B_4 for this system has been estimated by Monte Carlo methods.[16] We give the results below. In four dimensions the quantity v_0 has the value $1/2$.[17]

$$\begin{aligned}
B_1 &= 1\\
B_2 &= \pi^2\sigma^4/4 = 2.4674\\
B_3 &= B_2^2\left(4/3 - 3\sqrt{3}/2\pi\right) = 3.0826\\
B_4 &= B_2^3\left[\left(-3 + 2^{10}/45\pi^2\right) + \left(6 - 9\sqrt{3}/\pi - 173/180\pi^2\right) - 0.0949\right]\\
&= 2.2740
\end{aligned} \tag{5.1}$$

In addition we have calculated the first four b_n for the lattice gas with nearest-neighbor exclusion on the quartic lattice (analog of the simple cubic lattice in four dimensions). These coefficients are given in Table III.

Four coefficients is a very small number of terms. To see if even a rough estimate of ν might be expected from such a small set of data we calculated $\nu_{3\text{-d}}$ for spheres using the first four $\bar{b}_n$. The values of $\bar{z}_\sigma^{(-)}$ and ν resulting from this calculation are shown in Table IV. On comparing the value of ν calculated for spheres using four terms with that calculated using seven terms one sees that the estimate obtained using four terms is

Table IV. The Values of $\bar{z}_\sigma^{(-)}$ and ν Computed from $D \log \chi$ for the Models Discussed in the Text

Model	n^a	$-\bar{z}_\sigma^{(-)}$	ν
TR1 (2-d)	11	0.2706	1.188
		0.2707	1.191
		0.2706	1.189
TR12 (2-d)	9	0.2278	1.204
		0.2278	1.204
Disks (2-d)	7	0.1688	1.203
		0.1686	1.292
		0.1688	1.203
Quadratic (2-d)	15	0.2388	1.193
		0.2388	1.195
		0.2388	1.195
Q21 (2-d)	8	0.1948	1.193
		0.1948	1.192
fcc (3-d)	6	0.2573	1.043
		0.2573	1.042
sc (3-d)	11	0.1492	1.000
		0.1492	0.998
		0.1491	0.990
Spheres (3-d)	7	0.09138	1.015
		0.09129	1.005
		0.09138	1.015
Spheres (3-d)	4	0.09286	1.089
		0.09272	1.084
Quartic (4-d)	4	0.03138	1.025
		0.03118	1.008
Hyperspheres (4-d)	4	0.05181	1.014
		0.05143	0.995

[a] The quantity n is the number of $\bar{b}_n$ coefficients used.

adequate to obtain a rough idea of the magnitude of ν. The values of $\bar{z}_\sigma^{(-)}$ and ν for our two four-dimensional (4-d) models are also shown in Table IV. The value of $\nu_{4\text{-d}}$ seems to be about the same as that for 3-d systems, viz.

$$\nu_{4\text{-d}} \cong \upsilon_{3\text{-d}} \cong 1 \tag{5.2}$$

6. ONE-DIMENSIONAL MODELS

In one dimension the lattice gas with nearest-neighbor exclusion is exactly soluble.[18] The pressure per lattice site as a function of activity is given by the relation

$$\beta p = \ln \tfrac{1}{2}\left[1 + (1 + 4z)^{1/2}\right] \tag{6.1}$$

From (6.1) we can easily find the form of the singularity at $z_\sigma^{(-)}$ (switching from z to $\bar{z}$ with $v_0 = 1$):

$$\bar{\rho} = \frac{\partial \beta p}{\partial \ln \bar{z}} \sim -\left(\frac{1}{1 - \bar{z}/\bar{z}_\sigma^{(-1)}}\right)^{1/2}$$

$$\bar{z}_\sigma^{(-)} = -\tfrac{1}{2} \tag{6.2}$$

Using (6.2) we finally have

$$\chi \sim -\left(\frac{1}{1 - \bar{z}/\bar{z}_\sigma^{(-)}}\right)^{3/2} \tag{6.3}$$

and hence

$$\nu_{1\text{-}d} = 3/2 \tag{6.4}$$

The equation of state for hard rods in continuous space (the analog of disks or spheres for one dimension) is also known exactly.[19] For particles of unit length

$$\beta p = \rho/(1 - \rho) \tag{6.5}$$

The $B_n = 1$ for all n and hence (2.2) gives

$$z = \left(\frac{\rho}{1 - \rho}\right)\exp\left(\frac{\rho}{1 - \rho}\right) \tag{6.6}$$

Letting

$$y = -1/\rho \tag{6.7}$$

(6.6) becomes

$$\begin{aligned} z &= \left(\frac{-1}{1 + y}\right)\exp\left(\frac{-1}{1 + y}\right) \\ &= -\left(\frac{1}{e}\right)(1 - y + y^2 + \cdots)\left(1 + y - \frac{y^2}{2} + \cdots\right) \\ &= -\left(\frac{1}{e}\right)\left(1 - \frac{y^2}{2} + \cdots\right) \end{aligned} \tag{6.8}$$

Keeping only the lowest order term in y ($y \to 0$ as $\rho \to -\infty$) and solving for ρ, one obtains (6.2), and hence also (6.3), with $\bar{z}_\sigma^{(-)} = -(1/e)$.

Thus $\nu_{1\text{-d}} = 3/2$ is a universal result for all hard-particle systems in one dimension.

7. LATTICE GAS OF INDEPENDENT PARTICLES

The simplest lattice gas is where there is no interaction at all between particles on neighboring lattice sites, the only restriction on occupancy being that no two particles can occupy the same site. This is the lattice gas of independent particles. Since there is no interaction between particles it does not matter how the sites are arranged in space or on the dimensionality of space. In this simple model one can easily see why the b_n's must alternate in sign. If M is the number of lattice sites, then the number of ways of placing n identical particles on M sites (the discrete analog of the configuration integral) for the first few n's are

$$\begin{aligned} Q_1 &= M \\ Q_2 &= \frac{1}{2!} M(M-1) = -\frac{1}{2} M + \cdots \\ Q_3 &= \frac{1}{3!} M(M-1)(M-2) = \frac{1}{3} M + \cdots \\ Q_4 &= \frac{1}{4!} M(M-1)(M-2)(M-3) = -\frac{1}{4} M + \cdots \end{aligned} \tag{7.1}$$

The b_n are simply the coefficients of the term linear[10] in M. The generalization is

$$\beta p = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{1}{n} z^n = \ln(1+z) \tag{7.2}$$

giving

$$\begin{aligned} \rho &= \frac{z}{1+z} \\ \chi &= \frac{z}{(1+z)^2} \end{aligned} \tag{7.3}$$

Thus for the lattice gas of independent particles $\bar{z}_\sigma^{(-)} = -1$ and $\nu = 2$.

8. SUMMARY

Analysis of activity series indicates that the nature of the singularity on the negative activity axis in hard-particle systems containing approximately spherical particles depends only on the dimensionality of space. The exponents characterizing the divergence of the reduced compressibility at

$z_\sigma^{(-)}$ have been estimated to be

$$\begin{aligned} \nu_{\text{independent particles}} &= 2 \qquad \text{(exact)} \\ \nu_{\text{1-d}} &= 3/2 \qquad \text{(exact)} \\ \nu_{\text{2-d}} &= 1.195 \pm 0.005 \\ \nu_{\text{3-d}} &= 1.01 \pm 0.01 \end{aligned} \tag{8.1}$$

If we speculate that $\nu_{\text{2-d}} = 6/5$ and $\nu_{\text{3-d}} = 1$ exactly, then we have the following forms for the variation of the density near $z_\sigma^{(-)}$:

$$\begin{array}{ll} \text{independent} & \\ \text{particles} & \rho \sim -\Delta^{-1} \\ \text{1-d} & \rho \sim -\Delta^{-1/2} \\ \text{2-d} & \tau \sim -\Delta^{-1/5} \\ \text{3-d} & \rho \sim \ln \Delta \end{array} \tag{8.2}$$

where

$$\Delta = 1 - z/z_\sigma^{(-)} \tag{8.3}$$

The behavior of $\rho(z)$ near $z_\sigma^{(-)}$ for all the above expressions is qualitatively the same and is shown schematically in Fig. 2. Aside from determining the radius of convergence of activity series, the asymptote at $z_\sigma^{(-)}$ is important in determining the functional form of $\rho(z)$ as z enters the physical range (z

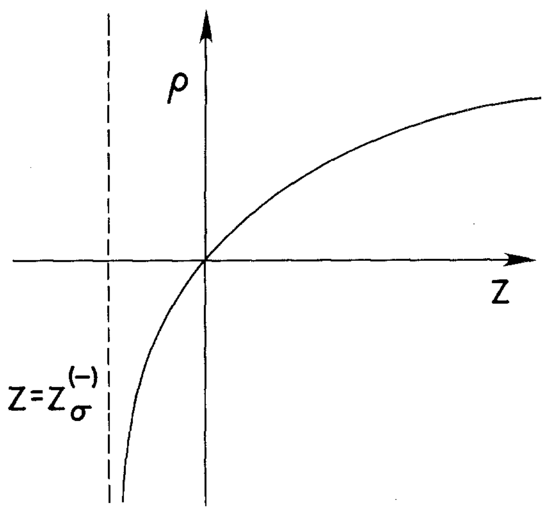

Fig. 2. Schematic illustration of the variation of $\rho(z)$ in the neighborhood of $z_\sigma^{(-)}$, the singularity on the negative z axis. The physical range of z is the positive axis.

positive and real). For independent particles, the singularity at $z_\sigma^{(-)}$ determines the functional form of $\rho(z)$ over the whole physical range of z, viz. $\rho = z/(1 + z)$.

REFERENCES

1. J. Groeneveld, *Phys. Lett.* **3**:50 (1962).
2. O. Penrose, *J. Math. Phys.* **4**:1312 (1963).
3. D. S. Gaunt and M. E. Fisher, *J. Chem. Phys.* **43**:2840 (1965).
4. D. S. Gaunt, *J. Chem. Phys.* **46**:3237 (1967).
5. M. W. Springgate and D. Poland, *Phys. Rev. A* **20**:1267 (1979).
6. R. M. Nisbet and I. E. Farquhar, *Physica* **76**:283 (1974).
7. B. J. Alder and T. E. Wainwright, *J. Chem. Phys.* **33**:1439 (1960); *Phys. Rev.* **127**:359 (1962).
8. M. F. Sykes, J. W. Essam, and D. S. Gaunt, *J. Math. Phys.* **6**:283 (1965); M. F. Sykes, D. S. Gaunt, S. R. Mattingly, J. W. Essam, and C. J. Elliott, *J. Math. Phys.* **14**:1066 (1973).
9. J. Orban and A. Bellemans, *J. Chem. Phys.* **49**:363 (1968).
10. M. W. Springgate and D. Poland, *J. Chem. Phys.* **62**:680 (1975).
11. J. S. Rowlinson, *Mol. Phys.* **7**:593 (1964); P. C. Hemmer, *J. Chem. Phys.* **42**:1116 (1965).
12. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**:939 (1964); *J. Chem. Phys.* **46**:4181 (1967); K. W. Kratky, *Physica* **85A**:607 (1976); *J. Chem. Phys.* **69**:2251 (1978).
13. L. Boltzmann, *Amsterdam Ber.*, 477 (1899); H. Happel, *Ann. Phys. (Leipzig)* **30**:246 (1906); R. Majumdar, *Bull. Calcutta Math. Soc.* **21**:107 (1929).
14. K. W. Kratky, *Physica* **87A**:584 (1977).
15. M. Luban and A. Baram, *J. Chem. Phys.* **76**:3233 (1982); C. G. Joslin, *J. Chem. Phys.* **77**:2701 (1982).
16. F. H. Ree and W. G. Hoover, *J. Chem. Phys.* **40**:2048 (1964).
17. H. F. Blichfeldt, *Math. Ann.* **101**:605 (1929); *Math. Z.* **39**:1–15 (1935); J. Leech, *Can. J. Math.* **16**:657 (1964).
18. D. Poland and H. A. Scheraga, *Theory of Helix-Coil Transitions in Biopolymers* (Academic Press, New York, 1970), Chap. 10.
19. L. Tonks, *Phys. Rev.* **50**:955 (1936); K. F. Herzfeld and M. G. Mayer, *J. Chem. Phys.* **2**:38 (1934).