

Rigid Disks and Spheres at High Densities. III

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A formal derivation of an asymptotic expansion for the Helmholtz free energy F_N of a system of N ν -dimensional rigid spheres of diameter σ is given, which has the form,

$$F_N/Nk_B T \sim \nu \ln(\lambda/\sigma) - \nu \ln(\tau-1) + C + D(\tau-1) + E(\tau-1)^2 + \dots,$$

where k_B is Boltzmann's constant, λ is the mean thermal de Broglie wavelength, and $\tau = V/V_0$ is the reduced volume of a system of volume V , close-packed volume V_0 , at temperature T . Formal expressions for the constants C , D , and E are derived, and the cell-cluster technique is applied to the calculation of C and D for the hexagonal-close-packed and face-centered-cubic lattices. The results are

$$C_{\text{HCP}} = 1.7786846\dots,$$

$$C_{\text{FCC}} = 1.7795003\dots,$$

$$D_{\text{HCP}} = 0.54187\dots,$$

$$D_{\text{FCC}} = 0.557994\dots$$

A value for D for the two-dimensional triangular lattice is found to be

$$D_T = 0.098993\dots$$

Agreement with computer experiments is generally good.

I. INTRODUCTION

A rigorous series development of the high-density thermodynamic properties, analogous to the low-density virial expansion, is not yet known. However, some progress has been made toward establishing the asymptotic form, at high densities, of the free energy for the special case of hard-core models.¹⁻³ Hard-core models allow one to introduce a natural parameter of smallness, namely

$$\alpha = \tau - 1,$$

with

$$\tau = V/V_0, \quad (\text{I.1})$$

where V_0 is the close-packed value of the volume V . On the basis of computer calculations,⁴ it was first suggested that α was an appropriate expansion parameter and that the leading asymptotic term in the pressure was the free-volume expression. The validity of this asymptotic expression for finite systems has been proven^{1,2} and for certain special models one could^{2,3} prove it for the thermodynamic limit $N \rightarrow \infty$.

Despite the lack of a rigorous proof of validity in the

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¹ Z. W. Salsberg and W. W. Wood, *J. Chem. Phys.* **37**, 798 (1962).

² W. G. Hoover, *J. Chem. Phys.* **40**, 937 (1964); **43**, 371 (1965); **44**, 221 (1966).

³ M. E. Fisher, *J. Chem. Phys.* **42**, 3852 (1965).

⁴ B. J. Alder, W. G. Hoover, and T. E. Wainwright, *Phys. Rev. Letters* **11**, 241 (1963).

thermodynamic limit, we have in a series of articles⁵⁻⁷ used what we believe is a correct asymptotic expansion for the thermodynamic properties of rigid-disk and rigid-sphere systems in the limit $V \rightarrow V_0$. This expansion gives the following form for the Helmholtz free energy, F_N , for a classical system of N ν -dimensional particles:

$$\frac{F_N}{Nk_B T} \sim \nu \ln \frac{\lambda}{\sigma} - \nu \ln(\tau-1) + C + D(\tau-1) + E(\tau-1)^2 + \dots \quad (\text{I.2})$$

The diameter of a ν -dimensional rigid sphere is denoted by σ , $\lambda = (h^2/2\pi m k_B T)^{1/2}$ is the mean thermal de Broglie wavelength for spheres of mass m , T is the absolute temperature and k_B is Boltzmann's constant.

In the past only the constant C has been formulated in terms of molecular properties. In Sec. II of this paper we give a formal derivation of Eq. (I.2) and obtain explicit expressions for the constants C , D , and E . In Sec. III we use the cell cluster techniques developed earlier^{5,6} to estimate C and D for the hexagonal-close-packed (HCP) and face-centered-cubic (FCC) packings of rigid spheres. The results are summarized in Sec. IV. In the earlier papers in this series^{5,6} the constant C for a two-dimensional system of rigid disks was estimated

⁵ F. H. Stillinger, Jr., Z. W. Salsberg, and R. L. Kornegay, *J. Chem. Phys.* **40**, 1564 (1964).

⁶ Z. W. Salsberg, W. G. Rudd, and F. H. Stillinger, Jr., *J. Chem. Phys.* **47**, 4534 (1967).

⁷ F. H. Stillinger, Jr., and Z. W. Salsberg, *J. Chem. Phys.* **46**, 3962 (1967).

using cell clusters with five or fewer particles. In Appendix B of this paper we present a calculation of the constant D for rigid disks using cell clusters of four or fewer particles. Appendix A is devoted to an outline of the coordinate systems used in the three dimensional hard-sphere calculations.

Recent computer experiments⁸⁻¹⁰ on finite systems provide experimental data from which estimates of the constants C , D , and E can be obtained. Comparison of these results and our cell-cluster estimates are given in Sec. V.

II. AN ASYMPTOTIC EXPANSION FOR THE FREE ENERGY

The petit canonical ensemble Helmholtz free energy, $F_N(V, T)$, for a system of N ν -dimensional rigid spheres contained in a ν -dimensional volume V at temperature T is given by

$$F_N = -k_B T \ln Q_N(V, T), \tag{II.1}$$

$$Q_N = (\lambda^{\nu N} N!)^{-1} \int_V \dots \int_V \prod_{i < j} H(r_{ij} - \sigma) \prod_{i=1}^N d\mathbf{r}_i, \tag{II.2}$$

where $H(x)$ denotes the unit step function,

$$H(x) = 0 \text{ if } x < 0 \\ = 1 \text{ if } x \geq 0, \tag{II.3}$$

and r_{ij} is the distance between the centers of the ij pair of spheres.

It is convenient to begin by making a transformation of coordinates that puts all the volume dependence explicitly in the unit step functions. We define the volume per particle

$$v = V/N$$

and introduce the reduced variables

$$\mathbf{x}_i = \zeta \mathbf{r}_i, \\ \zeta = v^{-1/\nu}. \tag{II.4}$$

Then Q_N can be written in the form

$$Q_N = (\lambda^{\nu N} N!)^{-1} v^N \int_{\omega} \dots \int_{\omega} \prod_{i < j} H(x_{ij} - \zeta \sigma) \prod_{i=1}^N d\mathbf{x}_i. \tag{II.5}$$

We assume that when the volume is varied, its shape is held fixed so that ω is a fixed volume, independent of V , with

$$\int_{\omega} d\mathbf{x}_i = N.$$

The entire reduced configuration space, $\mathbf{x} = \{\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N\}$, can be divided into $N!$ equivalent nonover-

lapping regions, $\mathcal{R}_l, l=1, \dots, N!$. The detailed prescription for this division can be found in Ref. 5. In summary, however, one spans the volume ω by a virtual lattice of N sites and each region \mathcal{R}_l is characterized by having each particle associated with a definite lattice site. In this paper we neglect vacancies or other imperfections. The symmetry of the problem then enables us to write

$$Q_N = \lambda^{-\nu N} v^N \int \dots \int \prod_{i < j} H(x_{ij} - \zeta \sigma) \prod_{i=1}^N d\mathbf{x}_i. \tag{II.6}$$

\mathcal{R}_l

Let $\mathbf{x}_i^{(0)}$ denote the lattice site associated with particle i and introduce the displacements \mathbf{y}_i of each particle away from its lattice site

$$\mathbf{x}_i = \mathbf{x}_i^{(0)} + \mathbf{y}_i. \tag{II.7}$$

We immediately note that when $v = v_0$, the close-packed volume, all the $\mathbf{y}_i = 0$ and for nearest-neighbor pairs only

$$x_{ij}^{(0)} = \sigma \zeta^0. \tag{II.8}$$

Since we are concerned with the high-density limit, we think of the displacements \mathbf{y}_i as being small and expand x_{ij} in powers of

$$\mathbf{y}_ij = \mathbf{y}_j - \mathbf{y}_i, \tag{II.9}$$

$$x_{ij} = (\mathbf{x}_{ij} \cdot \mathbf{x}_{ij})^{1/2} = [(x_{ij}^{(0)})^2 + 2\mathbf{x}_{ij}^{(0)} \cdot \mathbf{y}_{ij} + \mathbf{y}_{ij}^2]^{1/2} \\ = x_{ij}^{(0)} + \mathbf{w}_{ij} \cdot \mathbf{y}_{ij} + \frac{1}{2}(x_{ij}^{(0)})^{-1} [\mathbf{y}_{ij} \cdot \mathbf{y}_{ij} - (\mathbf{w}_{ij} \cdot \mathbf{y}_{ij})^2] \\ + \frac{1}{2}(x_{ij}^{(0)})^{-2} (\mathbf{w}_{ij} \cdot \mathbf{y}_{ij}) [(\mathbf{w}_{ij} \cdot \mathbf{y}_{ij})^2 - \mathbf{y}_{ij}^2] + \dots, \tag{II.10}$$

where \mathbf{w}_{ij} is a unit vector defined by

$$\mathbf{w}_{ij} = \mathbf{x}_{ij}^{(0)} / x_{ij}^{(0)}.$$

A. High-Density Scaling

This development leads naturally to the scaled displacement coordinates

$$\mathbf{z}_j = \mathbf{y}_j / [\sigma(\zeta^0 - \zeta)]. \tag{II.11}$$

In view of Eq. (II.10), the arguments of the step functions in Eq. (II.6) have the following form in terms of the scaled variables:

$$x_{ij} - \zeta \sigma = \sigma(\zeta^0 - \zeta) [1 + \mathbf{w}_{ij} \cdot \mathbf{z}_{ij} + p_{ij}^{(1)} \epsilon + p_{ij}^{(2)} \epsilon^2 + O(\epsilon^3)], \tag{II.12}$$

where

$$p_{ij}^{(1)} = \frac{1}{2} [\mathbf{z}_{ij}^2 - (\mathbf{w}_{ij} \cdot \mathbf{z}_{ij})^2], \tag{II.13}$$

$$p_{ij}^{(2)} = \frac{1}{2} (\mathbf{w}_{ij} \cdot \mathbf{z}_{ij}) [\mathbf{z}_{ij}^2 - (\mathbf{w}_{ij} \cdot \mathbf{z}_{ij})^2], \tag{II.14}$$

and

$$\epsilon = (1 - \zeta / \zeta^0). \tag{II.15}$$

The parameter of smallness ϵ is related to $\alpha = \tau - 1$ as defined in Eq. (I.1) but at this stage of the development ϵ is a more convenient parameter to use.

Introducing the scaled coordinates, $\{\mathbf{z}_i\}$, into Eq. (II.6) and making use of the fact that $\zeta^0 - \zeta$ is always

⁸ B. J. Alder and T. E. Wainwright, J. Chem. Phys. **33**, 1439 (1960).

⁹ W. G. Hoover and B. J. Alder, J. Chem. Phys. **45**, 2361 (1966).

¹⁰ B. J. Alder, W. G. Hoover, and D. A. Young, J. Chem. Phys. **49**, 3688 (1968).

positive one can write

$$Q_N = [\sigma/\lambda]^{\nu N} [(\zeta^0/\zeta) - 1]^{\nu N} I_N(\epsilon), \quad (II.16)$$

$$I_N(\epsilon) = \int \cdots \int \prod_{i < j} H[1 + \mathbf{w}_{ij} \cdot \mathbf{z}_{ij} + p_{ij}^{(1)}\epsilon + p_{ij}^{(2)}\epsilon^2 + O(\epsilon^3)] d\mathbf{z}_1 \cdots d\mathbf{z}_N. \quad (II.17)$$

The high-density expansion for Q_N can now be obtained by expanding $I_N(\epsilon)$ in powers of ϵ

$$I_N(\epsilon) = I_N^{(0)} + I_N^{(1)}\epsilon + I_N^{(2)}\epsilon^2 + \cdots, \quad (II.18)$$

where

$$I_N^{(0)} = \int \cdots \int \prod_{i < j} H(1 + \mathbf{w}_{ij} \cdot \mathbf{z}_{ij}) d\mathbf{z}_1 \cdots d\mathbf{z}_N, \quad (II.19)$$

$$I_N^{(1)} = \int \cdots \int \left[\sum_{i < j} p_{ij}^{(1)} \delta(1 + \mathbf{w}_{ij} \cdot \mathbf{z}_{ij}) \right] d\Omega, \quad (II.20)$$

$$I_N^{(2)} = \int \cdots \int \left\{ \sum_{i < j} [2p_{ij}^{(2)} \delta(1 + \mathbf{w}_{ij} \cdot \mathbf{z}_{ij}) + (p_{ij}^{(1)})^2 \delta'(1 + \mathbf{w}_{ij} \cdot \mathbf{z}_{ij}) + \sum_{i < j} \sum_{k < l, i, j} p_{ij}^{(1)} p_{kl}^{(1)} \delta(1 + \mathbf{w}_{kl} \cdot \mathbf{z}_{kl}) \times \delta(1 + \mathbf{w}_{kl} \cdot \mathbf{z}_{kl}) \right\} d\Omega, \quad (II.21)$$

in which

$$d\Omega = \prod_{m < n} H(1 + \mathbf{w}_{mn} \cdot \mathbf{z}_{mn}) d\mathbf{z}_1 \cdots d\mathbf{z}_N$$

and $\delta'(x)$ is the derivative of the Dirac delta function $\delta(x)$.

From Eqs. (II.18), (II.16), and (II.1) we can obtain the corresponding expansion for the Helmholtz free energy

$$\frac{F_N}{Nk_B T} \underset{\epsilon \rightarrow 0}{\sim} \nu \ln \frac{\lambda}{\sigma} - \nu \ln \frac{\epsilon}{1 - \epsilon} + C' + D'\epsilon + E'\epsilon^2 + O(\epsilon^3), \quad (II.22)$$

where

$$C' = -N^{-1} \ln I_N^{(0)}, \quad (II.23)$$

$$D' = -(I_N^{(1)}/NI_N^{(0)}), \quad (II.24)$$

$$E' = -N^{-1} [(I_N^{(2)}/I_N^{(0)}) - \frac{1}{2} (I_N^{(1)}/I_N^{(0)})^2]. \quad (II.25)$$

B. Expansion in Terms of $\tau - 1$

At this point we now introduce the parameter α [see Eq. (I.1)] since the results of the computer experiments^{9,10} have been analyzed in this manner. Since

$$\epsilon = 1 - \tau^{-1/\nu}$$

or

$$\alpha = (1 - \epsilon)^{-\nu} - 1$$

one obtains

$$F_N/Nk_B T \underset{\tau \rightarrow 1}{\sim} \nu \ln(\lambda/\sigma) - \nu \ln \alpha + C + D\alpha + E\alpha^2 + \cdots, \quad (II.26)$$

where the coefficients C , D , and E bear the following relation to the coefficients in Eq. (II.22):

$$C = C' + \nu \ln \nu,$$

$$D = (D'/\nu) + \frac{1}{2}(\nu - 1),$$

$$E = \frac{E'}{\nu^2} - \frac{1}{2} D' \frac{\nu + 1}{\nu^2} + \frac{1}{24} \frac{(1 + 2\nu)(1 - \nu)}{\nu}. \quad (II.27)$$

The equation of state is obtained from the thermodynamic relation¹¹

$$P = -(\partial F_N / \partial V)_{T, N}$$

and can be written in the form

$$\kappa = PV/Nk_B T = \nu/\alpha + C_0 + C_1\alpha + \cdots, \quad (II.28)$$

where

$$C_0 = \nu - D$$

and

$$C_1 = -(D + 2E), \quad (II.29)$$

etc.




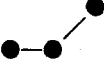


III. CELL-CLUSTER ANALYSIS

For earlier high density calculations^{5,6} a sequence of approximations, based upon an exact product representation⁵ for the partition function, was developed. One starts with the single-particle free-volume theory and evaluates correction factors due to the correlated motion of larger and larger sets of contiguous particles. The product representation for the partition function is equivalent to a series expansion for the Helmholtz free energy and one may regard this sequence as successive additive corrections to the Helmholtz function.⁶ It is important to emphasize that this sequence of approximations, while well defined, is not unique and does not correspond to any known convergent series. The extension of the method to formulate a sequence of approximations for C , D , etc., is also not unique. One procedure which we have not explored would be to develop a sequential series of approximations for each of the integrals, $I_N^{(0)}$, $I_N^{(1)}$, and $I_N^{(2)}$, introduced in Eq. (II.18). An alternative method, which was adopted, is described below.

First span the system by a virtual lattice and consider all possible sets of lattice sites which can be

¹¹ The question which arises is whether or not one is justified in differentiating the asymptotic series for F_N to obtain the asymptotic form for the pressure. This is a difficult question to answer, and we have no rigorous justification. For a discussion of this point the reader should consult Ref. (3) where Fisher shows that, because the pressure is known to be a nonincreasing function of the volume, it is possible to establish an asymptotic form for the pressure if one has appropriate upper and lower bounds on the free energy.

TABLE I. The clusters and their contributions to C for the face-centered cubic lattice. If we choose one of the planes stacked as ABC ABC \dots , then \bullet represents a particle in the plane and \circ represents a particle above or below the plane.

Cluster graph	(n, t)	$g(n, t)$	$C_{n,t}$
	1, 1	1	1.56296891460
	2, 1	6	0.02745684623
	3, 1	6	0.00857927082
	3, 2	24	0.00294232690
	3, 3	12	-0.00055793886
	3, 4	8	-0.00815972303

connected using nearest-neighbor bonds. We classify each set according to the number of sites n and the configuration t and call it a cluster of type (n, t) . Examples of such clusters are given in the accompanying tables for small values of n .

Next consider the particles associated with these lattice sites. For each set (n, t) we fix the $N-n$ particles, not associated with the n sites of the cluster, at their lattice positions. We then compute the partition function, $Q_{n,t}$, for the n particles in the cluster and from this obtain the corresponding free energy

$$F_{n,t}/k_B T = -\ln Q_{n,t}. \tag{III.1}$$

With these results in mind one defines a series of functions $W_{n,t}$ by means of the following recursion relations:

$$W_{1,1} = F_{1,1}/k_B T, \tag{III.2}$$

$$W_{n,t} = \frac{F_{n,t}}{k_B T} - \sum_{l=1}^{n-1} \sum_s \eta_{n,t}^{l,s} W_{l,s} \quad n \geq 2, \tag{III.3}$$

where $\eta_{n,t}^{l,s}$ is the number of subclusters of type (l, s) in the cluster (n, t) .¹² For a macroscopic system of N particles, the total free energy takes the following form,

$$\frac{F_N}{N k_B T} = \sum_{n=1}^N \sum_t g(n, t) W_{n,t}, \tag{III.4}$$

where $N g(n, t)$ is the number of different ways the cluster (n, t) can be formed in the system of N particles.

The high density expansion procedure outlined in Sec. II can be applied to the free energy for each cluster. Corresponding to Eq. (II.22) one obtains

$$\frac{F_{n,t}}{k_B T} \underset{\epsilon \rightarrow 0}{\sim} n\nu \ln \frac{\lambda}{\sigma} - n\nu \ln \frac{\epsilon}{1-\epsilon} + C_{n,t}^* \epsilon + D_{n,t}^* \epsilon^2 + \dots, \tag{III.5}$$

¹² The reader who is not familiar with this method is referred to Refs. 5 and 6 where specific examples of the coefficients $\eta_{n,t}^{l,s}$ are given for the two-dimensional triangular lattice.

in which $C_{n,t}^*, D_{n,t}^*$, etc.,¹³ are evaluated in terms of the corresponding integrals for this cluster

$$\begin{aligned} C^* &= -\ln I_{n,t}^{(0)}, \\ D^* &= -I_{n,t}^{(1)}/I_{n,t}^{(0)}, \\ E^* &= -[(I_{n,t}^{(2)}/I_{n,t}^{(0)}) - \frac{1}{2}(I_{n,t}^{(1)}/I_{n,t}^{(0)})^2]. \end{aligned} \tag{III.6}$$

The integrals $I_{n,t}^{(j)}$ ($j=0, 1, 2, \dots$) are obtained by applying Eqs. (II.19), (II.20), and (II.21) to the system specified by the cluster (n, t) . Using Eq. (III.5) and the recursion relations, Eqs. (III.2) and (III.3), for the free energy one can obtain corresponding recursion relations involving the coefficients C^*, D^* , etc. For example let

$$C_{1,1} = C_{1,1}^* \tag{III.7}$$

$$C_{n,t} = C_{n,t}^* - \sum_{l=1}^{n-1} \sum_s \eta_{n,t}^{l,s} C_{l,s}, \quad n \geq 2. \tag{III.8}$$

In a similar manner let

$$D_{1,1} = D_{1,1}^*, \tag{III.9}$$

$$D_{n,t} = D_{n,t}^* - \sum_{l=1}^{n-1} \sum_s \eta_{n,t}^{l,s} D_{l,s}, \quad n \geq 2, \tag{III.10}$$

and

$$E_{1,1} = E_{1,1}^* \tag{III.11}$$

$$E_{n,t} = E_{n,t}^* - \sum_{l=1}^{n-1} \sum_s \eta_{n,t}^{l,s} E_{l,s}, \quad n \geq 2. \tag{III.12}$$

Thus the functions $W_{n,t}$ also have a high-density asymptotic expansion of the form

$$W_{1,1} = \nu \ln \frac{\lambda}{\sigma} - \nu \ln \frac{\epsilon}{1-\epsilon} + C_{1,1} + D_{1,1} \epsilon + E_{1,1} \epsilon^2 + \dots, \tag{III.13}$$

$$W_{n,t} = C_{n,t} + D_{n,t} \epsilon + E_{n,t} \epsilon^2 + \dots. \tag{III.14}$$

Equation (III.13) also represents $F_{1,1}/k_B T$ for the single-particle free-volume model. The asymptotic form of the free energy can now be reconstructed using Eq. (III.4). One obtains for the constants C', D' , etc., defined in Eq. (II.22) the following result

$$C' = \sum_{n=1}^N C_n' \tag{III.15}$$

with

$$C_n' = \sum_t g(n, t) C_{n,t} \tag{III.16}$$

and

$$D' = \sum_{n=1}^N D_n' \tag{III.17}$$

¹³ Note that C^*, D^* , and E^* are defined as extensive quantities as opposed to the general coefficients in Eq. (II.22) which are intensive in character. The combinatorial nature of the cell-cluster development requires the extensive character of these intermediate quantities.

with

$$D_n' = \sum_t g(n, t) \mathcal{D}_{n,t} \quad (III.18)$$

E' can be analyzed in an analogous manner.

IV. RESULTS

Tables I-III give the cluster graphs and results for $\mathcal{C}_{n,t}$ [defined in Eqs. (III.7) and (III.8)] through clusters of three particles ($n \leq 3$) for the face-centered-cubic and hexagonal-close-packed lattices, and for $\mathcal{D}_{n,t}$ [defined in Eqs. (III.9) and (III.10)] through two-particle clusters ($n \leq 2$) for both lattices. The calculations of the cluster integrals were done on the Rice Computer, using a non-numerical integration technique, and were shown to be correct to within round-off errors of machine accuracy (10 decimal figures).

TABLE II. The clusters and contributions to C for the hexagonal close-packed lattice. If we choose one of the AB AB ... planes (perpendicular to the usual c axis) to be the basal plane, then \bullet , \circ , and \times represent spheres in, above and below the plane, respectively. The solid lines indicate movable (versus fixed) nearest neighbors.

Cluster graph	(n, t)	$g(n, t)$	$\mathcal{C}_{n,t}$
	1, 1	1	1.56296891460
	2, 1	3	0.02745684623
	2, 2	3	0.02709231482
	3, 1	1	-0.01753174048
	3, 2	1	0.00084474576
	3, 3	6	-0.00811789336
	3, 4	3	0.00885792681
	3, 5	12	0.00288449204
	3, 6	12	-0.00055750733
	3, 7	6	0.00294233502
	3, 8	6	0.00681407836
	3, 9	3	0.00147549105

TABLE III. The contributions to D for both the face-centered and hexagonal lattices. The description of the clusters is the same as in the previous tables.

Cluster graph	(n, t)	$g(n, t)$	$\mathcal{D}_{n,t}$
Face-centered cubic			
	1, 1	1	-0.375
	2, 1	6	-0.15850285
Hexagonal-close-packed			
	1, 1	1	-0.375
	2, 1	3	-0.15886729
	2, 2	3	-0.18969355

The results, grouped as noted in Eqs. (III.3), (III.15), and (III.17) according the value of n , are

$$C_{FV} = 1.562968 \dots, \quad (IV.1)$$

$$C_{FCC} = C_{FV} + 0.164741 \dots + 0.051790 \dots$$

$$= C_{FV} + 0.21653 \dots, \quad (IV.2)$$

$$C_{HCP} = C_{FV} + 0.163647 \dots + 0.052068 \dots$$

$$= C_{FV} + 0.215716 \dots \quad (IV.3)$$

or

$$C_{FCC} = 1.7795003 \dots, \quad (IV.4)$$

$$C_{HCP} = 1.7786846 \dots, \quad (IV.5)$$

$$C_{HCP} - C_{FCC} = -0.000816, \quad (IV.6)$$

where HCP, FCC, and FV denote the hexagonal-close-packed and face-centered-cubic lattices, and the single-particle free-volume, respectively.

Similarly, the results for D , which we call the first curvature correction [see Eq. (III.18)], are

$$D_{FV} = 0.87500, \quad (IV.7)$$

$$D_{FCC} = D_{FV} - 0.317006 \dots = 0.557994 \dots, \quad (IV.8)$$

$$D_{HCP} = D_{FV} - 0.333127 \dots = 0.541873 \dots, \quad (IV.9)$$

and

$$D_{HCP} - D_{FCC} = -0.016120. \quad (IV.10)$$

The reader is referred to Appendix B for results concerning the D term for the two dimensional triangular lattice.

For the value of C_0 in Eq. (II.28)

$$C_0^{HCP} = 2.458127, \quad (IV.11)$$

$$C_0^{FCC} = 2.442006. \quad (IV.12)$$

V. DISCUSSION

Unfortunately, the complexity of the cell cluster integrals prohibits the convenient extension of our calculations to include larger clusters. The current

TABLE IV. Summary of the constants in the high-density forms for the Helmholtz free energy and equation of state for rigid disks and rigid spheres.

Method	2D triangular lattice			3D FCC lattice			3D HCP lattice		
	Free energy ^a		Eq. of state ^b C_0	Free energy ^a		Eq. of state ^b C_0	Free energy ^a		Eq. of state ^b C_0
	C-C _{FV}	D-D _{FV}		C-C _{FV}	D-D _{FV}		C-C _{FV}	D-D _{FV}	
Cell cluster	-0.011 ^c	-0.345 ^d	1.90 ^d	+0.2165 ^e	+0.5580 ^f	2.442 ^f	+0.2157 ^g	+0.5419 ^g	2.458 ^g
Molecular dynamics ^h	-0.06±0.02	...	1.86±0.03	0.24±?	...	2.56±0.02
Monte Carlo ^b	-0.05±0.01	+0.216±0.015	+0.216±0.02

^a See Eq. (II.26) for definitions of C and D. Subscript FV refers to the single particle free-volume model.

^b See Eq. (II.28) for definition of C_0 .

^c Value obtained from all clusters with five or fewer particles.

^d Value obtained from all clusters with four or fewer particles.

^e Value obtained from all clusters with three or fewer particles.

^f Value obtained from the one and two particle clusters only.

^g See Ref. 10.

^h See Ref. 16.




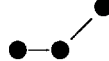







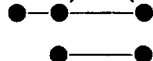
values for C and D indicate that the HCP lattice structure is slightly more stable than the FCC lattice, and that there is no polymorphic phase transition in the high-density region. The FCC and HCP lattices are very similar in their thermodynamic properties, as was previously expected⁸ and recently verified.¹⁰

The expansion (I.2) correctly predicts the observed^{14,15} free-volume dependence of the pressure upon the density. The entropies of the systems

$$S_N = -(\partial F_N / \partial T)_{V,N} \quad (\text{V.1})$$

are found to be $\simeq 0.2Nk$ lower than those predicted by the Lennard-Jones-Devonshire theory. This is in good agreement with the computer experiments,¹⁰ in which the additive entropy constant related to C in Eq. (I.2) is obtained by integrating the pressure volume curve, assuming a position for the melting point. The limiting

TABLE V. The clusters and results for disks in a triangular lattice.

Cluster graph	(n, t)	g(n, t)	$\mathcal{D}_{n,t}$
	1, 1	1	-0.11111
	2, 1	3	-0.20922
	3, 1	3	-0.25522
	3, 2	6	-0.02406
	3, 3	2	+0.10913
	4, 1	3	-0.00355
	4, 2	12	-0.00370
	4, 3	6	-0.00320
	4, 4	6	-0.00176
	4, 5	2	-0.00790
	4, 6	12	+0.00397
	4, 7	3	-0.00116

¹⁴ N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. 21, 1807 (1953).

¹⁵ M. N. Rosenbluth and A. W. Rosenbluth, J. Chem. Phys. 22, 881 (1954).

entropy has also been calculated by Hoover and Ree¹⁶ by means of a Monte Carlo calculation for a "single-occupancy" system which eliminates the need to estimate a position for the melting tie line. A summary of the various results can be found in Table IV. Included in this table are our values of the equation of state constant C_0 [see Eqs. (IV.11) and (IV.12)] which agree well with the experimental values^{10,16} for the two- and three-dimensional lattices, respectively. The cell-cluster calculation for C_0 through four-particle clusters can be found in Appendix B.

APPENDIX A: COORDINATE SYSTEMS

The reader is referred to Refs. 17 and 18 for an analysis of the coordinate systems used in the two-dimensional triangular and three-dimensional face-centered-cubic lattices, respectively. We present here an outline of the approach used for the hexagonal-close-packed structure.

We define a set of lattice basis vectors \mathbf{a}_1 , \mathbf{a}_2 , and \mathbf{a}_3 and express the relative displacement vector as

$$\mathbf{z}_{ij} = q\mathbf{a}_1 + v\mathbf{a}_2 + s\mathbf{a}_3. \quad (\text{A.1})$$

In terms of this basis, the nearest-neighbor unit vectors \mathbf{w}_{ij} are as follows:

$$\begin{aligned} \mathbf{w}_1 &= -\mathbf{w}_2 = \mathbf{a}_1/a \\ \mathbf{w}_3 &= -\mathbf{w}_4 = \mathbf{a}_2/a \\ \mathbf{w}_5 &= -\mathbf{w}_6 = (\mathbf{a}_2 - \mathbf{a}_1)/a \\ \mathbf{w}_7 &= \mathbf{a}_3/a \\ \mathbf{w}_8 &= (\mathbf{a}_3 - \mathbf{a}_1)/a \\ \mathbf{w}_9 &= (\mathbf{a}_3 - \mathbf{a}_2)/a \\ \mathbf{w}_{10} &= (\frac{2}{3}\mathbf{a}_1 + \frac{2}{3}\mathbf{a}_2 - \mathbf{a}_3)/a \\ \mathbf{w}_{11} &= (-\frac{1}{3}\mathbf{a}_1 + \frac{2}{3}\mathbf{a}_2 - \mathbf{a}_3)/a \\ \mathbf{w}_{12} &= (\frac{2}{3}\mathbf{a}_1 - \frac{1}{3}\mathbf{a}_2 - \mathbf{a}_3)/a. \end{aligned} \quad (\text{A.2})$$

We now introduce the reciprocal lattice basis vectors, \mathbf{b}_1 , \mathbf{b}_2 , and \mathbf{b}_3 defined by

$$\mathbf{b}_i \cdot \mathbf{a}_j = a\delta_{ij}, \quad (\text{A.3})$$

where δ_{ij} is the Kronecker delta. In this basis

$$\mathbf{z}_{ij} = t\mathbf{b}_1 + u\mathbf{b}_2 + v\mathbf{b}_3 \quad (\text{A.4})$$

and the transformation $(t, u, v) \rightarrow (x, y, z)$, the Cartesian coordinates, has Jacobian

$$J = \sqrt{2}.$$

APPENDIX B: CURVATURE CORRECTION FOR THE TWO-DIMENSIONAL TRIANGULAR LATTICE

Table V shows the cluster graphs and results for the triangular lattice through clusters of four disks. The results are as follows:

$$D_{\text{FV}} = 0.4444 \dots$$

$$D = D_{\text{FV}} - 0.294315 \dots - 0.022905 \dots - 0.0282275 \dots$$

$$= D_{\text{FV}} - 0.345447 \dots$$

$$D = 0.098993 \dots \quad (\text{B.1})$$

This yields, for the constant term in the equation of state [Eq. (II.25)]

$$C_0 = 1.9010 \dots \quad (\text{B.2})$$

as compared with

$$C_0 = 1.86 \pm 0.03 \quad (\text{B.3})$$

from molecular dynamics⁴ and

$$C_0 = 1.888$$

from the correlated cell model.⁴

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¹⁶ W. G. Hoover and F. H. Ree, *Bull. Am. Phys. Soc.* **12**, 1141 (1967); *J. Chem. Phys.* **49**, 3609 (1968).

¹⁷ W. G. Rudd and Z. W. Salsburg, *J. Chem. Phys.* **45**, 1026 (1966).

¹⁸ W. G. Rudd, *J. Chem. Phys.* **48**, 619 (1968).