

High Density Hard Square Particles Approaching a Close Packed "Brickwall" Configuration

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Received November 3, 1970

Recently Beyerlein, Rudd, Salsburg, and Buynoski [1] obtained the following asymptotic expansion for the Helmholtz free energy F_N of a high density system of N hard squares with a side of length σ ,

$$\frac{F_N}{Nk_B T} \underset{\uparrow \rightarrow 1}{\cong} 2 \ln \left(\frac{\lambda}{\sigma} \right) - 2 \ln(\uparrow - 1) + C + D(\uparrow - 1) + E(\uparrow - 1)^2 + \dots, \quad (1)$$

where k_B is the Boltzmann constant, λ is the mean thermal de Broglie wavelength $(h^2/2\pi m k_B T)^{1/2}$, the density parameter \uparrow is the ratio of the system area to the close-packed system area, and C, D, \dots are constant parameters. The parameters D, E, \dots are coefficients in the expansion of $2 \ln(\uparrow^{1/2} + 1)$ in powers of $(\uparrow - 1)$. Beyerlein, Rudd, Salsburg, and Buynoski [1] estimated C with the modified cell cluster method to be -0.26044 for a hard square solid whose particles approach the points of a square lattice in the neighborhood of close packing. Hoover suggested an alternative "brickwall" high density structure might be a more stable structure [1] and if so would be a more appropriate model for a nearly close packed hard square solid. A comparison of an accurate estimate of C for the "brickwall" structure with the value obtained assuming a square lattice structure would resolve this question. It is therefore the purpose of this note to present some results obtained for C assuming a "brickwall" structure.

For a nearly closed packed system of N hard squares with fixed boundary conditions the partition function Q_N can be written as [1]

$$Q_N = \left(\frac{\sigma}{\lambda} \right)^{2N} (\uparrow^{1/2} - 1)^{2N} Z_N, \quad (2)$$

$$Z_N = \int_{\infty}^{\infty} \dots \int_{\infty}^{\infty} \prod_{i < j} \phi_{ij} \prod_1^N du_k dv_k.$$

* Financial support from the Department of Chemistry and Geology of Clemson University is acknowledged.

The coordinates u_k and v_k are scaled displacement coordinates defined by

$$\begin{aligned} u_k &= x_k/(a - \sigma), \\ v_k &= y_k/(a - \sigma), \end{aligned} \quad (3)$$

where x_k and y_k are displacements of particle k from its associated lattice site along cartesian axis parallel to the sides of the square particles, and a is the component of distance between neighboring lattice sites along one of the cartesian axis. The ϕ_{ij} are the Boltzmann factors for interactions between particles i and j . For the "brickwall" configuration each particle may interact with 6 neighbors in the neighborhood of the closed packed limit and the ϕ_{ij} are:

$$\phi_{ij} = \phi[1 \pm (u_j - u_i)] \quad (4)$$

for interactions along the x axis and

$$\phi_{ij} = \phi[1 \pm (v_j - v_i)] \quad (5)$$

for interactions along the y coordinate. The symbol ϕ represents the unit Heaviside function. The upper sign is used in Eq. (4) if the position of the lattice site for particle j relative to that for particle i along the x axis is positive and the lower sign if it is negative. A similar sign convention holds for Eq. (5) except in this case the y component of the relative displacement of the lattice sites is considered. Since we have formally extended the limits of integration to $\pm\infty$, the integrand includes ϕ_{ij} representing upper and lower bounds on the particle displacements imposed by the boundaries of the system. These are obtained from Eqs. (4) and (5) by fixing the boundary particle at its lattice site ($u_j = 0$, $v_j = 0$) yielding:

$$\begin{aligned} \phi_{ij} &= \phi(1 - u_i), \\ \phi_{ik} &= \phi(1 - v_i), \end{aligned} \quad (6)$$

for upper bounds on the displacement of particle i , and

$$\begin{aligned} \phi_{ji} &= \phi(1 + u_i), \\ \phi_{ki} &= \phi(1 + v_i), \end{aligned} \quad (7)$$

for lower bounds on the displacement of particle i . Two different subscripts j and k are used for the boundary particles to indicate upper bounds in the x direction are provided by different boundary particles from those in the y direction. The additive free energy constant C is obtained from Z_N by the following equation:

$$C = 2 \ln 2 - N^{-1} \ln Z_N. \quad (8)$$

Since it is presently not possible to calculate C for a large system, the modified cell cluster expansion developed by Salsburg and coworkers [1-4] is used to estimate C . The expansion makes use of a quantity $C_{n,\alpha}$ given by

$$C_{n,\alpha} = 2 \ln 2 - n^{-1} \ln Z_{n,\alpha}, \quad (9)$$

where $Z_{n,\alpha}$ is defined for clusters of n contiguous particles whose lattice site configuration is identified by subscript α in the same way as Z_N is defined by Eq. (2) for N particles. Graphical representations of the lattice configuration for all clusters through four particles are illustrated in Table I for the "brickwall" lattice configuration. Solid lines connecting two particles in the cluster means the full side of each particle opposes the other and a dashed line implies only half a side of each particle opposes the other. The expression for C in terms of the cell cluster series is

$$C = C_{1,1} + \sum_{n=2}^N \sum_{\alpha} t(n, \alpha) W_{n,\alpha}, \quad (10)$$

where $t(n, \alpha)$ is the number of ways the graph (n, α) may be placed on the point lattice associated with the N particle system and $W_{n,\alpha}$ are calculated from the following sequence of recursion relations:

$$\begin{aligned} 2C_{2,1} &= 2C_{1,1} + W_{2,1}, \\ 2C_{2,2} &= 2C_{1,1} + W_{2,2}, \\ 3C_{3,1} &= 3C_{1,1} + 2W_{2,1} + W_{3,1}, \\ &\vdots \quad \quad \quad \vdots \\ nC_{n,\alpha} &= nC_{1,1} + \sum_{m=2}^n \sum_s \eta_{m,\beta}^{n,\alpha} W_{m,\alpha}, \end{aligned} \quad (11)$$

$$(12)$$

which is a general expression for the recursion relation, where $\eta_{m,\beta}^{n,\alpha}$ is the number of ways graph (m, β) may be placed on the lattice sites of graph (n, α) .

Values of $Z_{n,\alpha}$ were calculated exactly using integration by parts [5]. The results for $Z_{n,\alpha}$ and $W_{n,\alpha}$ are listed in Table I. The values given in Table I for $t(n, \alpha)$ neglect boundary effects and thus represent the value obtained in the thermodynamic limit.

From data in Table I all terms contributing to the C series may be summed up through $n = 4$ to yield

$$C = 0.0 + 0.14925 - 0.13898 - 0.03418 \dots, \quad (13)$$

where the first term is the free volume value of C and the second, third, and fourth

TABLE I

The cluster graphs and their respective values for
 $t(n, \alpha)$, $Z_{n,\alpha}$ and $W_{n,\alpha}$









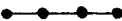
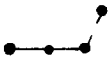














Graph	(n, α)	$t(n, \alpha)$	$Z_{n,\alpha}$	$W_{n,\alpha}$
	(1, 01)	1	4	0.0
	(2, 01)	1	18	-0.11779
	(2, 02)	2	14	0.13352
	(3, 01)	1	$\frac{256}{3}$	-0.05212
	(3, 02)	4	63	0.0
	(3, 03)	2	60	-0.08471
	(3, 04)	2	48	0.02064
	(3, 05)	2	48	0.02064
	(4, 01)	1	$\frac{1250}{3}$	-0.02953
	(4, 02)	4	$\frac{896}{3}$	0.0
	(4, 03)	4	$\frac{2560}{9}$	0.0
	(4, 04)	2	$\frac{441}{2}$	0.0
	(4, 05)	2	$\frac{441}{2}$	0.0
	(4, 06)	2	$\frac{8235}{32}$	-0.00079
	(4, 07)	4	$\frac{819}{4}$	0.00469

TABLE I (Continued)

Graph	(n, α)	$t(n, \alpha)$	$Z_{n,\alpha}$	$W_{n,\alpha}$
	(4, 08)	1	192	-0.00047
	(4, 09)	4	216	0.0
	(4, 10)	4	216	0.0
	(4, 11)	2	$\frac{567}{2}$	0.0
	(4, 12)	4	204	-0.01228
	(4, 13)	2	164	0.00347
	(4, 14)	4	164	0.00347
	(4, 15)	2	164	0.00347
	(4, 16)	2	216	0.0

terms are corrections for all 2 particle, three particle and four particle correlations, respectively. The estimate of C up through four particle correlations is -0.02391 . Comparison with the value, -0.26544 , estimated for C through four particle contributions assuming a square lattice configuration [1], indicates the square lattice configuration is more stable. Calculations are in progress to estimate C for the "brickwall" configuration through 5 particle contributions to be compared with -0.26044 obtained to the same order of approximation for the square lattice configuration [1]. However, the apparent rate of convergence of the cell cluster series is fast enough, so that it is doubtful comparison of higher order estimates of C will change the above conclusion on the relative stability of the square lattice and "brickwall" configurations.

Many of the $Z_{n,\alpha}$ values are a combination of products and quotients of those obtained for lower order clusters. This is reflected in Table I by a value of zero for $W_{n,\alpha}$. This greater simplicity of the "brickwall" lattice might make it in some ways a preferred model for studying correlations in hard particle systems.

ACKNOWLEDGMENTS

The author is deeply indebted to the late Professor Z. W. Salsburg for the initial ideas and inspiration leading to this work on hard particle systems and other work the author is pursuing in statistical mechanics. The author's association with Professor Salsburg has been invaluable and he very regretfully accepts the loss of a teacher and a friend.

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