Critical exponent for glassy packing of rigid spheres and disks

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A simple conjecture on the behavior of the canonical ensemble partition function for a system of rigid spheres and disks, as random close packing is approached, is supported in a suggestive manner by definite trends that emerge from "derivative-logarithm" analyses of the low-density virial series with the presently known coefficients. The conjecture predicts that the inverse pressure at *random* close packing should become zero with infinite slope, whereas it very probably does so with finite slope as the *ordered* closest-packing limit is approached.

I. INTRODUCTION

The packing of rigid spheres and disks—in appearance a mere academic problem—is of great importance[1] in physics, chemistry, biology, metallurgy, ceramics, and soil science as well as in many branches of engineering. It is fundamental in the microscopic theory of fluids, glasses (or amorphous solids) and crystals. On the other hand, sphere packings are crucial in determining the macroscopic granular nature of powders and other porous materials.[2] Disk packings are important in the structure of monomolecular films.

Packings of identical spheres in *regular* arrangements have been known for a long time to give packing fractions $\eta \equiv \rho\pi\sigma^3/6$, where ρ is the number density and σ the hard-sphere diameter, which are $\pi/6 \simeq 0.52$ for simple-cubic packing and $\sqrt{3}\pi/8 \simeq 0.68$ for body-centered cubic. The face-centered cubic (fcc) is one of an infinite number[3] of structures, called primitive hexagonal, all with identical packing fractions, presumed[4] to be the *closest* or densest possible packing, with the value $\sqrt{2}\pi/6 \simeq 0.74$. In two dimensions $\eta = \rho\pi\sigma^2/4$, and there are only two regular close packings: square packing with $\eta = \pi/4 \simeq 0.79$, and triangular (or hexagonal) packing with $\eta = \pi/2\sqrt{3} \simeq 0.91$ which is the closest possible packing.

Irregular (dense) close packing, also known as random close packing (RCP), appears to occur at a single, unique density value—at least in three dimensions. Perhaps the best empirical determination[5] of the RCP density in three dimensions comes from actual laboratory experiments involving shaking carefully prepared containers filled with up to 80 000 steel ball bearings. Extrapolation of the measured densities then serves to eliminate finite-size effects. The most reliable packing fraction thus extrapolated for three-dimensional RCP is probably 0.6366 ± 0.0004, as obtained by Finney.[6] Note that $2/\pi = 0.636\,619\,77\ldots$ and that π is now in the denominator, not the numerator, in contrast to the regular close packings mentioned above. The *two*-dimensional random-close-packing fraction, on the other hand, is much more uncertain. Using lucite disks Stillinger *et al.*[7] arrive at the ratio $x_{\mathrm{RCP}} \equiv \eta_{\mathrm{RCP}}/(\pi/2\sqrt{3}) = 0.90 \pm 0.01$, which we have independently confirmed by experimenting with pennies on a tabletop. Berryman[8] surveys an extensive list of both laboratory experiments and computer simulations which yielded values for x_{RCP} between 0.87 to 0.98.

Both ordered and disordered packings are characterized by a diverging pressure which is easily understood in terms of the impenetrability of the hard sphere or disk particles: for either system and at either close packing an infintesimal increase in density would require application of an infinite pressure. Extrapolation techniques based on the first seven known[9] virial coefficients of the low-density expansion for the pressure of a hard-sphere system suggest the presence of *both* divergences: Padé approximants point[10] to the irregular, whereas Levin-type extrapolants appear to suggest[11] *regular* packing pressure divergences. Both methods, however, have been limited to predicting only *first-order*-pole—type divergences, i.e., with a critical exponent of unity, in agreement with the free-volume approximation[12] of *regular* close packing which becomes exact in one dimension. A logarithmic divergence (zero critical exponent) has been conjectured[13] in the two-dimensional hard-disk case.

The Padé approach is extended in this paper to include the possibility of any real value for the critical exponent at random close packing. In Sec. II we discuss the problem in terms of the canonical ensemble pressure and propose a conjecture for the critical exponent α being bounded as $0 < \alpha < 1$. This is corroborated in Sec. III by means of suggestive trends which emerge from so-called derivative-logarithm series analyses based on the low-density virial expansion in powers of the density. Section IV presents a discussion of our numerical results.

II. CANONICAL ENSEMBLE PRESSURE

The pressure in the canonical ensemble is given by[14]

$$P=-(\partial f/\partial v)_T \qquad (1)$$

with $\rho\equiv 1/v=V/N$, the volume per particle and f the Helmholtz free energy per particle. The latter is defined as

$$f=-kT \lim_{\substack{N,V\to\infty \\ (v \text{ fixed})}} [N^{-1}\ln Q(N,V,T)] \qquad (2)$$

with k being Boltzmann's constant and T the absolute temperature. The classical canonical ensemble partition function $Q(N,V,T)$ for a ν-dimensional system of N particles of mass m contained in volume V, at temperature T, and interacting pairwise through the potential function $\phi(r)$ is

$$Q(N,V,T)=\lambda^{-\nu N}(N!)^{-1}\int_V d^\nu r_1 \int \cdots \int_V d^\nu r_N \exp\left[-\sum_{\substack{i,j=1 \\ i<j}}^{N}\phi(r_{ij})/kT\right],$$
$$\lambda\equiv h/\sqrt{2\pi mkT}\ . \qquad (3)$$

For the special case of *rigid* particles of diameter σ (rods, disks, spheres, etc.) $\phi(r_{ij})=\infty$ $(r_{ij}<\sigma)$ and $=0$ $(r_{ij}>\sigma)$ so that (3) becomes

$$Q(N,V,T)=\lambda^{-\nu N}Z(N,V)\ , \qquad (4)$$

$$Z(N,V)\equiv(N!)^{-1}\int_V d^\nu r_1 \cdots \int_V d^\nu r_N \prod_{\substack{i,j=1 \\ i<j}}^{N}\theta(r_{ij}-\sigma)\ ,$$
$$\theta(x)\equiv\tfrac{1}{2}[1+\text{sgn}(x)]\ . \qquad (5)$$

In other words, the non-ideal-gas contribution to the equation of state (1) will be temperature independent because of (5), but still highly nontrivial in its density dependence. For the ideal gas $\phi=0$: $\pi\theta$ in (5) is replaced by unity and $Z(N,V)=V^N/N!$ immediately leads to $P=kT/v$.

The one-dimensional case of hard rods[15] readily[14] gives for (5) the result

$$Z(N,L)=[L-(N-1)\sigma]^N/N! \underset{\substack{N,L\to\infty \\ (L/N=v \text{ fixed})}}{\longrightarrow} e^N(v-\sigma)^N\ , \qquad (6)$$

where L is the length (volume) of the system, whence

$$P=kT/(v-\sigma)\ . \qquad (7)$$

As expected, the pressure clearly divergences as the density $\rho=1/v$ approaches the closest packing density $\rho_0\equiv 1/\sigma$. The divergence is a first-order pole.

In two and three dimensions P in fact also diverges at the closest packing specific volume $v_0=2\sqrt{3}/\pi$ (for $\nu=2$) and $v_0=6/\sqrt{2}\pi$ (for $\nu=3$). In both cases, by inspection of (5), $Z(N,V)\to 0$ as $v\to v_0^+$. Thus, it has been natural to assume, in light of the rigorous one-dimensional result (6), that the approach to zero of $Z(N,V)$ for dimension higher than one, is given by the power law

$$Z(N,V) \underset{N\gg 1,\ v\to v_0^+}{\longrightarrow} C(v-v_0)^\gamma\ ,\ \ \gamma>0 \qquad (8)$$

with C a density-independent positive constant. Together with (1), (2), and (4) this leads to the asymptotic pressure

$$P \underset{v\to v_0^+}{\longrightarrow} \frac{\gamma kT}{N(v-v_0)}\ , \qquad (9)$$

i.e., again to a first-order divergence at closest (regular) packing. It has further been conjectured[16] that, for very large N, $\gamma=\nu N$ so that (9) becomes

$$P \underset{v\to v_0^+}{\longrightarrow} \frac{\nu kT}{v-v_0} \qquad (10)$$

for any dimension ν, and of course reduces to (7) for $\nu=1$.

With all this in mind, we now return to the empirical fact mentioned above that P *also* diverges as hard-spheres or hard disks approach their respective (so-called Bernal) densities. ρ_B, which is *less than* the closest density ρ_0 by a few percent. That density value corresponds to dense (to distinguish from loose) random close packing (RCP). Since at this density value there occurs a *close,* but *not closest,* packing configuration, it is very conceivable that the integral in (5) may contribute with some *nonzero* positive constant. This allows one to conjecture that the so-called configuration integral in (5) behaves in that limit as

$$Z(N,V) \underset{N\gg 1,\ v\to v_B^+}{\longrightarrow} A+B(v-v_B)^{\beta N},\ \ \beta>0\ , \qquad (11)$$

where A, B, and β are arbitrary positive constants. The essential difference with the *closest* packing limit behavior (8) is, of course, the presence of the nonzero constant A allowing for the fact that at the Bernal density one has *close* but not closest packing, i.e., the polytope volume (5) is now not necessarily zero. Thence

$$P \underset{v\to v_B^+}{\longrightarrow} \frac{B}{A}\frac{\beta kT}{(v-v_B)^\alpha},\ \ 0<\alpha\equiv 1-\beta N<1\ ; \qquad (12)$$

in other words, P^{-1} approaches zero as $v\to v_B^+$ with *infinite* versus finite slope as it did before and as was obtained previously with Padé analyses.

Finally, we remark that a more general v dependence in the closest packing case (8) like, e.g., $e^{-D/(v-v_0)^\delta}$, with $D,\delta>0$, which also approaches zero as $v\to v_0^+$, will lead to $P^{-1}\sim(v-v_0)^{\delta+1}$; that is, to a greater-than-unit pole. On the other hand, in the RCP case replacing the $(v-v_B)^{\beta N}$ term in (11) by $e^{-E/(v-v_B)^\epsilon}$, with $E,\epsilon>0$, is easily seen to lead to *no* pressure divergence at all.

To conclude this section we display graphically the (first-order) pole placements produced by the Padé analysis of Ref. 10 based on the low-density virial expansion

$$P/\rho_0 kT \equiv xf(x) \underset{x\to 0}{\simeq} x(1+A_1x+\cdots+A_6x^6+\cdots)\,,$$
$$x\equiv\rho/\rho_0\,, \tag{13}$$
$$\rho_0\equiv\begin{cases}\sqrt{2}/\sigma^3 & \text{(fcc, 3D)}\\ 2/\sqrt{3}\sigma^2 & \text{(triangular, 2D)}\,,\end{cases}\quad A_n\equiv\rho_0^n B_{n+1}\,.$$

Here B_{n+1} is the well-known $(n+1)$st virial coefficient. In (13) only up to A_6 (or B_7) are known numerically.[9] For three dimensions (3D) there remains about a 4% error in A_6 and about 1% in A_5. All lower-order coefficients are known essentially errorless. In two dimensions, on the other hand, A_6 and A_5 are known[17] with errors which are just 0.44% and 0.005%, respectively.

The pole placements[10] of the different Padé approximants[18] $[L/M](x)$ to the sixth order polynomial in (13), with $1\le L+M\le 6$, are displayed in Fig. 1. The empirical three-dimensional Bernal density $x_B=\rho_B/\rho_0=6\eta_B/\pi\sqrt{2}\simeq 6\sqrt{2}/\pi^2\simeq 0.86$ is labeled as RCP in the figure, whereas the closest packing density $x=1$ is labeled fcc. The simplest nontrivial approximant $[0/1](x)$ to (13) just gives ($\hat{=}$ signifies "represented by")

$$P/\rho_0 kT \hat{=} x[0/1](x)\equiv\frac{x}{1-A_1x}\,,$$
$$A_1\equiv 2\sqrt{2}\pi/3\,, \tag{14}$$

which is *precisely* the van der Waals equation of state for a hard-sphere system, with A_1 the excluded volume per particle in units of $v_0\equiv\rho_0^{-1}$. The pole predicted at $x\simeq 0.34$ is plainly too far below the empirical $x_B\simeq 0.86$. In this respect, further approximants are clearly seen in Fig. 1 to improve. The highest-order, or maximal, approximants are indicated in boldface; of these the [2/4] and [3/3] reproduce the Bernal density to two-digit accuracy, namely, 0.8627 and 0.8622, respectively. We stress that the *central* values for A_5 and A_6, as quoted in Ref. 9, have been employed throughout.

We have come to realize that the results of this simple, or straight, Padé analysis may be fortuitous for two reasons: (i) use of other than the central values for A_5 and A_6 wildly moves the pole placements of Fig. 1, in some cases beyond the physical interval $0<x<1$, and (ii) a similar Padé analysis of the *two-* dimensional case,

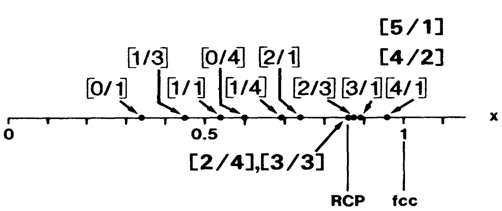

FIG. 1. Graphical display of pole placements of straight Padé analysis of virial series Eq. (13) for hard spheres according to Ref. 8. Boldfaced labels refer to maximum order approximants, i.e., which incorporate maximum available information of virial series.

where considerably smaller errors exist in A_5 and A_6, yields no clear cut suggestion of a RCP pole, even within the rather wide empirical range cited before of $0.87\le x_{\mathrm{RCP}}\le 0.98$. A possible reason for this may be that *straight* Padé analyses can only produce *first-* order poles; a more general treatment is now considered.

III. DERIVATIVE-LOGARITHM SERIES ANALYSES

In accordance with the conjectured critical exponent $0<\alpha<1$ of (12) one would expect $f(x)$ as defined in (13) to behave as

$$f(x)\underset{x\to x_B^-}{\sim}\frac{R}{(x_B-x)^\alpha} \tag{15}$$

in the neighborhood of the Bernal density, with R some positive constant. The method of the "derivative logarithm"[19] permits successively more accurate determination of both α and x_B, based only on the low-density virial expansion (13). Taking the natural log of (15) and then differentiating with respect to x gives

$$\ln f(x)\underset{x\to x_B^-}{\sim}\ln R-\alpha\ln(x_B-x)\,, \tag{16a}$$

$$\frac{d}{dx}\ln f(x)\underset{x\to x_B^-}{\sim}\frac{\alpha}{x_B-x}\,. \tag{16b}$$

Now, using (13) and expanding the log about $x=0$ leaves

$$\ln f(x)\underset{x\to 0}{\sim}\tilde{A}_1x+\tilde{A}_2x^2+\cdots+\tilde{A}_6x^6+\cdots\,, \tag{17}$$

where

$$\tilde{A}_1\equiv A_1,\quad \tilde{A}_2\equiv A_2-\tfrac{1}{2}A_1^2\,,$$
$$\tilde{A}_3\equiv(A_3-A_1A_2+\tfrac{1}{3}A_1^3),\ \ldots\,. \tag{18}$$

Differentiating (17) gives

$$\frac{d}{dx}\ln f(x)\underset{x\to 0}{\sim}A_1(1+C_1x+\cdots+C_5x^5+\cdots)\,,$$
$$C_n\equiv(n+1)\tilde{A}_{n+1}/A_1\quad(n=1,2,\ldots)\,. \tag{19}$$

A. Unbiased estimation

We attempt first to estimate, on the basis of information contained in the "virial" coefficients $A_1,A_2,\ldots,A_6$, both α *and* x_B. For this we combine (16b) and (19), yielding

$$\frac{\alpha}{x_B-x}\simeq\frac{d}{dx}\ln f(x)\simeq A_1(1+C_1x+\cdots+C_5x^5)\,. \tag{20}$$

The right-hand side (rhs) of this can now represented by Padé approximants

$$A_1[L/M](x)\equiv A_1P_L(x)/Q_M(x) \tag{21}$$

with $P_L(x)$, $Q_M(x)$ the Padé polynomials of order L and M in x, and $1\le L+M\le 5$. The real, positive zeros of $Q_M(x)$ will provide estimates for x_B. Subsequently, the corresponding value of α is extracted by combining (20) and (21) to give

TABLE I. Placement of zeros, x_B, of denominator polynomial in Padé approximants of Eq. (21) to low-density series defined in Eq. (20). Column marked α is associated critical exponent obtained from Eq. (22) and defined in Eq. (15). Entries marked with a dash related to [1/2] and [0/4] approximants are not given as the predicted x_B values are unreasonably large.

Order	$[L/M]$	x_B	α
5	[0/5]	0.9038	0.9644
	[1/4]	1.05	1.444
	[2/3]	0.7775	0.4411
	[3/2]	$(0.49+i0.59)$, c.c.	—
	[4/1]	1.09	3.252
4	[0/4]	1.245, 2.744	2.333, —
	[1/3]	1.154	1.772
	[2/2]	0.3370	0.0096
	[3/1]	0.4296	0.0314
3	[0/3]	1.015	1.372
	[1/2]	2.944	—
	[2/1]	Re<0	—
2	[0/2]	$(0.55+i1.09)$, c.c.	—
	[1/1]	Re<0	—
1	[0/1]	1.351	4.0

$$\alpha \hat{=} A_1[(x_B-x)P_L(x)/Q_M(x)]_{x=x_B} . \tag{22}$$

Table I lists the resulting values of x_B and α. We note that, without exception, (a) all x_B predicted within the physical interval $0<x_B<1$ are associated with a critical exponent $\alpha<1$, while (b) all x_B predicted outside this interval are always associated with $\alpha>1$. Even so, the results of this unbiased search are too scattered to reveal any additional meaningful trends. In order to pin down our predictions of α even further we fix x_B at the empirical value and then try to determine α.

B. Biased estimation

Multiplying (20) by (x_B-x) and rearranging the rhs we can write

$$\alpha \simeq x_B A_1(1+D_1x+\cdots+D_5x^5+\cdots) ,$$
$$D_n \equiv C_n - C_{n-1}/x_B \quad (n=1,2,\ldots) , \tag{23}$$

and insert for x_B the empirical value $\simeq 6\sqrt{2}/\pi^2 \simeq 0.8597$. The biased estimates for α then follow from Padé approximation to the rhs of (23); thus

$$\alpha \hat{=} x_B A_1[L/M](x_B) . \tag{24}$$

Table II lists the results, which are also displayed in Fig.

TABLE II. Critical exponent values α in two and three-dimensions resulting from biased method Eq. (24), as given by all Padé approximants $[L/M](x)$ to the low-density series Eq. (23). The value of x_B is fixed at the empirical values for random close packing of 0.8597 for hard spheres and 0.90 for hard disks.

		α	
Order	$[L/M]$	3D (with $x_B=0.8597$)	2D (with $x_B=0.90$)
5	[0/5]	0.8307	0.8374
	[1/4]	0.8165	0.1912
	[2/3]	0.7099	0.5166
	[3/2]	0.7364	0.4048
	[4/1]	0.8599	0.3762
	[5/0]	0.7975	0.5313
4	[0/4]	0.8665	0.9269
	[1/3]	1.557[a]	0.5771
	[2/2]	0.6557	0.5811
	[3/1]	2.1002	0.4683
	[4/0]	1.008	0.6274
3	[0/3]	1.0143	1.0416
	[1/2]	0.9591	0.4923
	[2/1]	0.2938	<0
	[3/0]	0.5035	0.7829
2	[0/2]	1.1455	1.2198
	[1/1]	3.4667[b]	1.6916[c]
	[2/0]	<0	1.0905
1	[0/1]	1.8681	1.5125
	[1/0]	1.6219	1.5030

[a]With pole at $x=0.613$.
[b]With pole at $x=0.439$.
[c]With pole at $x=0.282$.

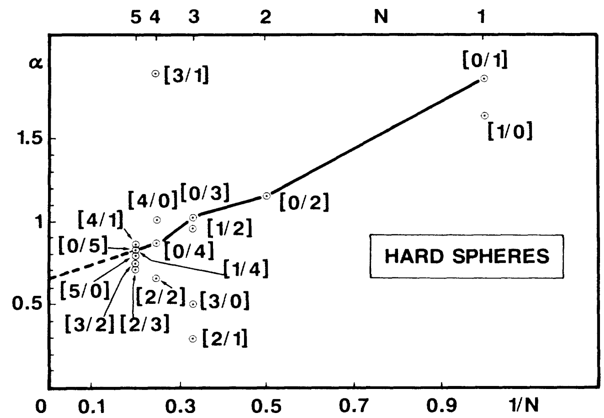

FIG. 2. Display of critical exponent values α predicted for hard spheres from biased method Eq. (24), plotted against inverse order $1/N$ of Padé approximants, where $N=L+M$.

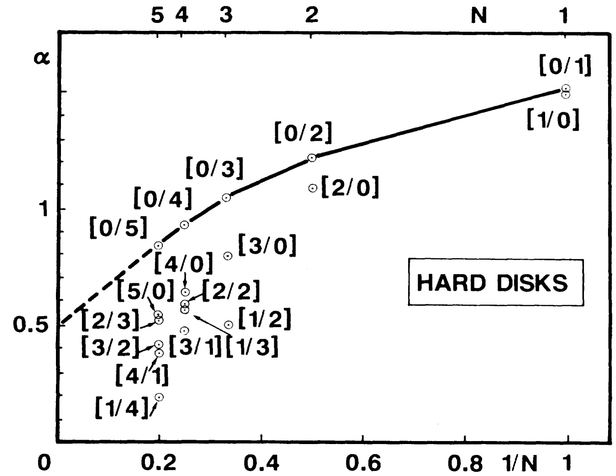

FIG. 3. Same as Fig. 2, but for hard disks.

2, where $N \equiv L+M$. All approximants are plotted except for the [1/1] and [1/3] which develop poles at some $x<x_B$, and the [2/0] which yields a *negative* value of α. Note that the highest-order approximants (with $L+M=5$) lie very close to each other, predicting an α in the range $0.6 \lesssim \alpha \lesssim 0.9$. The approximants $[0/N]$ are connected by straight-line segments only as a reference. Using $x_B=1$ in (23) instead of the empirical RCP value of 0.86 used above produces a similar plot except that now $1.2 \lesssim \alpha \lesssim 2$ for the highest-order approximants, a result tending to support the conjecture $\alpha=1$ for *ordered* closest packing, Eq. (10).

The results for two dimensions are also listed in Table II for the particular value of $x_B=0.90$. These are graphically displayed in Fig. 3, except for the approximants [1/1] and [2/1]. The latter predicts a negative, whereas the former develops a pole at $x<x_B$. Two well-defined trends are observed: (a) all approximants of order 4 or greater predict α in the conjectured range $0<\alpha<1$, and (b) the sequence of approximants $[0/N]$ $(N=1,2,\ldots,5)$ appears to provide an upper bound to all predicted real, positive α. Although extrapolation to $N\rightarrow\infty$ $(1/N\rightarrow 0)$ is very rough, it suggests a value of $\alpha \simeq \frac{1}{2}$. Similar extrapolations of the results using $x_B=0.87$ on the one hand, and $x_B=0.98$ on the other, yield, respectively, values of α of 0.36 and 0.78.

Finally, we mention that the first five Levin approximants[20] to (23) were also constructed for three-dimensions ($x_B=0.86$ and 1) and two-dimensions ($x_B=0.90$ and 1). They not only did not reveal acceptable trend behavior as in the Padé cases discussed above but produced, in roughly a third (7) of all cases (20), negative values for α.

IV. DISCUSSION

Based upon a simple conjecture regarding the asymptotic behavior of the canonical ensemble configuration integral for a classical system of rigid spheres or disks immediately leads one to a critical exponent α for the pressure divergence at random close packing which should lie in the interval $0<\alpha<1$.

It is argued that a possible reason for the failure of *straight* Padé analysis of the known virial series to shed any light on the Bernal density singularity is that these analysis, as carried out to date, *assume* a first-order singularity at that density.

A so-called "derivative-logarithm" analysis of the low-density virial expansion for the pressure is then carried out in the following two ways. (1) An " unbiased" form allowing both the pole placement (Bernal density) as well as the exponent to be estimated. This was illustrated in the three-dimensional case. (2) A "biased" scheme in which the Bernal density is fixed at its empirical value and the exponent predicted was illustrated in both three and two dimensions. Of course, no rigorous proof of the critical exponent conjecture is claimed, nor even of a uniquely calculated result, particularly since one disposes of only six coefficients in the series analyzed, versus the twenty or more in more traditional critical-exponent series-analyses work.[21]

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