Why is Random Close Packing Reproducible?

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We link the thermodynamics of colloidal suspensions to the statistics of regular and random packings. Random close packing has defied a rigorous definition yet, in three dimensions, there is near universal agreement on the volume fraction at which it occurs. We conjecture that the common value of $\phi_{\rm rcp} \approx 0.64$ arises from a divergence in the rate at which accessible states disappear. We relate this rate to the equation of state for a hard-sphere fluid on a metastable, noncrystalline branch.

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When Bernal turned to sphere packings as a route towards understanding liquids [1], he recognized the importance of the *random close-packing* (rcp) density, $\phi_{\rm rcp}$. This density was defined operationally to be the fraction of occupied volume in the densest disordered packing of hard spheres, determined by pouring, shaking, and kneading ball bearings in flasks and balloons [2,3]. Since then, these measurements have been reproduced by countless experiments and numerical algorithms, which find a common value of $\phi_{\rm rcp} \approx 0.64$ in three dimensions [4]. There are therefore many procedurally distinct but numerically consistent definitions of $\phi_{\rm rcp}$. In 1960, Bernal and Mason wrote, "The figure for the occupied volume of random close packing— 0.64—must be mathematically determinable, although so far as we know undetermined." [3]. Nearly 50 years later, a mathematically rigorous definition of rcp still remains elusive. Why should an ill-defined state have a reproducibly accepted value for its volume fraction?

Two approaches towards a rigorous definition have been suggested recently. A "random close-packed" state is ill defined because one can always obtain a denser state by introducing order into the system. This must be true because $\phi_{\rm rcp}$ is lower than the maximum close-packed density [5], $\phi_{\rm FCC} = \pi/3\sqrt{2} \approx 0.74$ of the face centered cubic (fcc) lattice. Torquato, *et al.* [6] proposed the "maximally random jammed" (MRJ) state defined by configurations with minimal values of typical order parameters, such as bond-orientational or crystalline order, which are "jammed," such that any particle or set of particles cannot be translated with respect to any of the rest of the particles in the system without introducing overlaps. Kansal, *et al.* [7] showed that several different order parameters yielded $\phi_{\rm MRJ} \approx 0.63$, close to $\phi_{\rm rcp}$. Nonetheless, one cannot calculate all possible order parameters, or determine that all order parameters yield the same MRJ packing fraction. Moreover, there may be a specific type of order associated with the MRJ state [8–11] that is maximal, though that metric is likely very different from those studied in [6].

A second approach is based on the energy landscape of systems of soft spheres. Specifically, O'Hern, *et al.* [11,12] considered potentials of the form

$$V(r) = \begin{cases} \epsilon(1 - r/\sigma)^{\alpha}/\alpha & r < \sigma \\ 0 & r \geq \sigma \end{cases}. \tag{1}$$

Here, ϵ is the characteristic energy of interaction and σ is the particle diameter. For $\alpha = 3/2$, 2 and 5/2, O'Hern, *et al.* studied the fraction of ideal gas states $f_0(\phi)$ belonging to basins of attraction of zero energy states or hard-sphere states (HSS) and found that $-df_0(\phi)/d\phi$, i.e., the rate at which the fraction of ideal gas states belonging to basins of attraction of HSS shrinks with increasing density, appears to develop a delta-function peak at $\phi_{\rm rcp}$ in the infinite system size limit [11,12]. This suggests that the majority of ideal gas states belong to basins of HSS that jam at $\phi_{\rm rcp}$. Here, a state is jammed if there are no zero frequency vibrational modes except for those due to floaters (particles with no overlapping neighbors) or overall translation and rotation of the system [13]. The uncertainty in this approach is associated with how the energy landscape is explored [14,15]; different algorithms may yield different final energy minima for a given ideal gas state.

Here we exploit a relation between the pressure—a thermodynamic quantity that can be measured for colloidal suspensions—and the behavior of hard-sphere packings. In particular, we show that the fractional rate at which allowed states disappear with increasing volume fraction is proportional to the pressure. We find that free volume theory provides a reasonable fit to the equation of state of the hard-sphere liquid, with a single fit parameter $\phi_{\rm max} = 0.640 \pm .006$, corresponding to the density at which the pressure diverges, in excellent agreement with $\phi_{\rm rcp}$. We conclude by discussing these results in the context of previous work and making some conjectures regarding the origin of the reproducibility of $\phi_{\rm rcp}$.

We first derive a useful relation between the pressure and the rate at which allowed states disappear. This relation is used to calculate pressure in simulations [16]; here, we use it to gain insight into the packings of hard spheres of volume v. The probability of finding an allowed hard-sphere state at number density ρ is $\mathcal{R}(\rho) \equiv Z_{\rm HS}(\rho)/Z_{\rm IG}(\rho)$, where $Z_{\rm HS}$ and $Z_{\rm IG}$ are the numbers of allowed configurations (i.e., the canonical partition functions) for hard spheres and for an ideal gas of point particles, respectively. We now consider the effect of increasing the density of a particular state at density ρ. The probability of *not* finding a new state at $\rho + \delta\rho$, given this state at ρ, is $J(\rho)\delta\rho$, where $J(\rho) = -\frac{1}{\mathcal{R}}\frac{\partial\mathcal{R}}{\partial\rho}$. Using the thermodynamic definition of pressure, $p \equiv T\partial \ln Z/\partial V$, we find

$$J(\phi) = \frac{V}{\phi T}[p_{\mathrm{HS}}(\phi) - \phi T/v]. \tag{2}$$

where $\phi = \rho v$, p_{HS} and $\phi T/v = p_{\mathrm{IG}}$ are the pressures of the hard-sphere and ideal gas systems, respectively, V is the volume, T is the temperature ($k_B = 1$).

In Fig. 1(a) we show the experimentally measured equation of state for a hard-sphere system (circles) [17]. The pressure increases until $\phi = \phi_X \approx 0.49$, at which point fluid and crystal coexist. Eventually, both $p_{\mathrm{HS}}(\phi)$ and $J(\phi)$ diverge at ϕ_{FCC}, signaling an inability to construct any higher density states, i.e., close packing. Thus, if all the states are counted in Z_{HS}, J does not diverge until ϕ_{FCC}.

There is also a metastable branch of the equation of state that is reproducibly measurable numerically (see Fig. 1) [18,19] and potentially measurable experimentally in rapidly sedimented colloidal suspensions [20]. This branch is used to study the colloidal glass transition [21] and dynamics in granular media [22]. Along this branch, the pressure apparently diverges [18,19] at ϕ_{rcp} as $p_{\mathrm{HS}}(\phi) \sim (\phi_{\mathrm{rcp}} - \phi)^{-1}$. Such a divergence is predicted on the basis of polytope theory, or free volume theory, for classical hard spheres [8,23]. According to Eq. (2), J diverges there. To construct an analytical approximation to a metastable branch that continues smoothly from ϕ_X to a divergence at some $\phi_{\max}$, we turn to free volume theory. To calculate the free energy, we must construct the Voronoi tesselation for each packing [24]. For a given packing, each sphere is allowed to independently explore the free volume of its cell. The free energy involves a sum over all possible tesselations and requires knowledge of the distribution of free volumes [25]. However, if ϕ is decreased infinitesimally near $\phi_{\max}$, the increase in free volume of each cell for an affine rarefaction of the packing scales as $[(\phi_{\max}/\phi)^{1/3} - 1]^3$. Thus, sufficiently near $\phi_{\max}$, the pressure is independent of tesselation and depends on only one parameter, $\phi_{\max}$ itself:

$$p_{\mathrm{FV}} = -\frac{T\phi^2}{v}\frac{d}{d\phi}\ln\{[(\phi_{\max}/\phi)^{1/D} - 1]^D\}, \tag{3}$$

where D is the dimension of space [24]. Note that as the volume fraction further decreases, the geometry of the allowed volume will change and, though the scaling factor remains the same, the prefactor will change, leading to additional corrections. Recent arguments [26] based on statistical geometry suggest that Eq. (3) should be approximately correct for the metastable branch.

Figure 1(a) shows that free volume theory provides a very reasonable fit to the equilibrium liquid branch of the data of Ref. [17] just below ϕ_X, with $\phi_{\max} \approx 0.64$ in 3D, in excellent agreement with measured rcp values. The inset shows that Δ, the mean-squared error, is a strong function of $\phi_{\max}$. We find a comparable value of $\phi_{\max} \approx 0.636$ when we fit the range $\phi \in [0.3, 0.5]$ to the first ten virial coefficients [27]. Unsurprisingly, we also find a similar value ($\phi_{\max} \approx 0.635$) when we fit to the Carnahan-Starling approximate equation of state [28]. The latter function is known to describe experimental or numerical measurements of the liquid branch of the equation of state to within measurement error [17,29–31]. It is worth noting that the fitted values of $\phi_{\max}$ are insensitive to the region over which we fit the data. Using the entire equilibrium liquid branch $\phi \in [0, 0.5]$ only changes $\phi_{\max}$ in the last

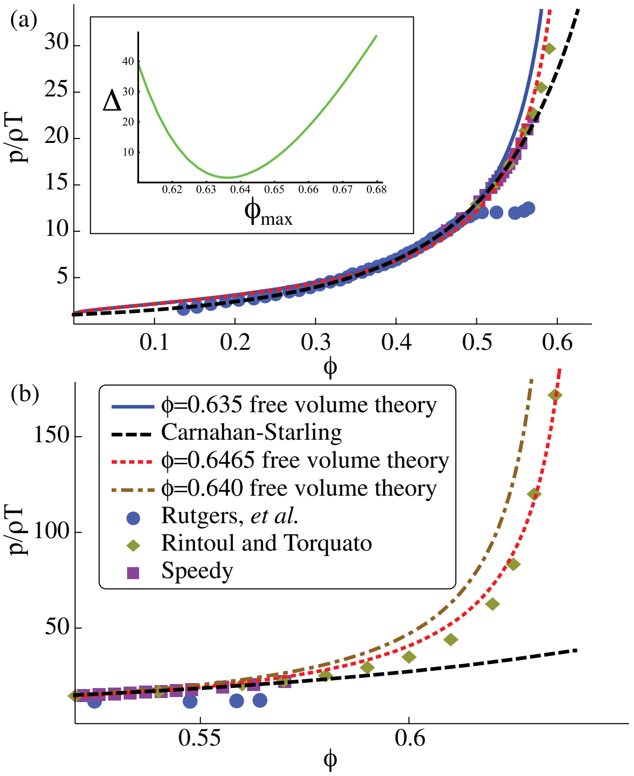

FIG. 1 (color online). Measured equation of state p (in units of ρT) versus volume fraction ϕ for a hard-sphere fluid from experiments by Rutgers *et al.* [17] (circles) and simulations by Rintoul and Torquato [18] (diamonds) and Speedy [19] (squares). The dashed curve is the Carnahan-Starling equation of state. In (a) we show two fits to free volume theory, corresponding to $\phi_{\max} = 0.635$ (solid), which is the best fit to the experimental data for the equilibrium liquid branch, and $\phi_{\max} = 0.6465$ (dotted), which is the best fit to the numerical data for the metastable branch. In (b) we show free volume theory for $\phi_{\max} = 0.6465$ (dotted) and $\phi_{\max} = 0.640$ (solid). Part (a) of the figure shows the quality of the fit to the equilibrium liquid branch while part (b) shows the quality of the fit to the metastable branch. Inset to (a): the variation in the mean-square error Δ between free volume theory and the experimental data as a function of $\phi_{\max}$.

decimal place (for example, we obtain $\phi_{\max} \approx 0.637$ when fitting to the Carnahan-Starling equation over the whole range). Additionally, Aste and Coniglio [32] have estimated the pressure in free volume theory and find a branch of the equation of state diverging at $\phi_{\max} \approx 0.65$.

We have also fit free volume theory to numerical measurements of the metastable branch [18,19] and find a best fit for $\phi_{\max} \approx 0.6465$—less than 2% higher than that for the equilibrium liquid branch. In Fig. 1 we plot Eq. (3) for the various best fit values of $\phi_{\max}$; these curves are nearly indistinguishable in terms of their ability to fit the equilibrium portion of the curve. Note that our one-parameter fit reproduces not only the shape of the divergence but the overall amplitude of the pressure quite well. The range of fit values is reasonably represented by $\phi_{\max} = 0.640 \pm 0.006$.

We now note that the many different algorithms and preparation methods that yield $\phi_{\mathrm{rcp}} \approx 0.64$, have one point in common: they all contrive to avoid crystallization and should thus correspond to a metastable branch of the pressure. For two very different approaches, conjugate gradient minimization [11,12] and the Lubachevsky-Stillinger algorithm [8,33], there is good evidence that the accessible states follow the branch estimated in Fig. 1. Both procedures yield a pair correlation function $g(r)$ that diverges at contact as $|\phi_{\mathrm{rcp}} - \phi|^{-1}$, implying a likewise diverging pressure. These approaches both observe a catastrophic loss of states; i.e., they jam, at ϕ_{rcp}, consistent with Eq. (2).

These results suggest that ϕ_{rcp} is a divergent end point of a metastable branch of the equation of state. This provides another way of thinking about why rcp has not been a well-defined concept [6]. Metastable branches are somewhat arbitrary; to obtain them, one must introduce constraints that exclude certain states (e.g., crystalline states) from the partition function [34]. Different constraints lead to different metastable branches. Alternatively, one can think in terms of the Andreev-Fisher droplet model [35,36], or the instanton approach to first-order transitions [37], which predict an essential singularity at ϕ_X. This essential singularity precludes analytic continuation of the pressure beyond ϕ_X; physically, droplets of the nucleating crystalline phase prevent the clean definition of the metastable branch.

The possibility of multiple metastable branches is supported by the existence of multiple divergent end points, found via the Lubachevsky-Stillinger algorithm [6]. In this algorithm, one starts with an equilibrium liquid configuration at low volume fraction and compresses by increasing the diameters of all the particles at some rate Γ [33]. The system jams at some packing fraction $\phi_f(\Gamma)$ which approaches ϕ_{rcp} from above as $\Gamma \rightarrow \infty$, suggesting that metastable branches may end at any $\phi \in [\phi_{\mathrm{rcp}}, \phi_{\mathrm{fcc}}]$.

What is special about metastable branches ending at ϕ_{rcp}? One possibility is that the MRJ state [6] may be generalizable to an entire MRJ metastable branch of the pressure that ends at ϕ_{rcp}. This is the philosophy underlying calculations of Rintoul and Torquato [18], who followed a metastable branch by discarding all states with appreciable values of the bond-orientational order parameter and found a diverging pressure at ϕ_{rcp}.

Another not inconsistent possibility is that ϕ_{rcp} is better defined than the metastable branch that it terminates. In this scenario, ϕ_{rcp} corresponds to a singularity of the free energy that is inaccessible in equilibrium due to an essential singularity at ϕ_X, the onset of crystallization. Indeed, exact analyses of one-dimensional models show that it is possible for a system to have a metastable branch that is not well defined but that ends in a divergent end point that is a true singularity [38].

We therefore conjecture that ϕ_{rcp} represents a special well-defined divergent end point of a set of metastable branches of the pressure. Any procedure that samples a nonzero fraction of states belonging to metastable branches with this end point will yield a divergent pressure, and therefore a divergent rate at which states disappear. This would explain why so many different procedures, all sampling states somewhat differently, yield the same value of ϕ_{rcp}. At the same time, it is clear that other procedures might yield different jamming densities by avoiding states belonging to metastable branches ending at ϕ_{rcp}. Parisi and Zamponi [39,40] have suggested a similar but more elaborate scenario. There, ϕ_{rcp} is the divergent end point of a metastable branch, but there is another point on the branch, $\phi_g < \phi_{\mathrm{rcp}}$, which marks a thermodynamic glass transition. Above ϕ_g, the configurational entropy vanishes; the system must remain in the lowest free energy states and the relaxation time is infinite.

A singularity in the rate of change of number of states does not necessarily imply that most initial states will flow to ϕ_{rcp}. Most states might have their jamming thresholds at values of $\phi < \phi_{\mathrm{rcp}}$, leaving only a few that terminate at ϕ_{rcp}. Numerical results suggest that the opposite might be true. Indeed, they suggest that ϕ_{rcp} may not only mark a well-defined divergent end point of a set of metastable equations of state, but that an even stronger condition might hold: the distribution of jamming thresholds may actually have a maximum at ϕ_{rcp}. This conjecture is motivated by results of O'Hern, *et al.* [11,12], which suggest that for several soft repulsive potentials, the overwhelming number of ideal gas states belong to basins of attraction of HSS that have their jamming thresholds at ϕ_{rcp}. Note that the probability of belonging to a basin of attraction of a state with a jamming threshold at ϕ depends on both the size distribution of basins of attraction and the distribution of jamming thresholds. For small systems, Xu, *et al.* [41] have separated the these two distributions by explicitly enumerating the jamming thresholds; their results suggest that the distribution of jamming thresholds is maximal near ϕ_{rcp}, consistent with this conjecture. While it is unlikely that the maxima of the distributions of jamming thresholds and of jamming thresholds weighted by their basin of attractions and the divergent end point of the metastable branch all coincide at exactly the same density, it is possible that they agree with $\phi = 0.64$ to within 1%–2%, so that any one of these could constitute a clean definition of $\phi_{\rm rcp}$ [42].

We note that $\mathcal{R}(\phi)$ includes states both at their jamming thresholds and *below* their jamming thresholds. We have argued that the form of the equilibrium equation of state suggests that at $\phi_{\rm rcp}$, the latter states completely dwarf the number of HSS that are at their jamming thresholds, hiding the divergence in the pressure. It is only when these more ordered states are excluded by restricting the system to a metastable branch of the pressure that a signature of $\phi_{\rm rcp}$ appears. This reasoning suggests that a clean definition of $\phi_{\rm rcp}$ will rely not only on the distribution of jamming thresholds, but the *number* of allowed HSS at their jamming thresholds at $\phi_{\rm rcp}$ as a function of system size [43].

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