


Quasicrystal of Binary Hard Spheres on a Plane Stabilized by Configurational Entropy

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Because of their aperiodic nature, quasicrystals are one of the least understood phases in statistical physics. One significant complication they present in comparison to their periodic counterparts is the fact that any quasicrystal can be realized as an exponentially large number of different tilings, resulting in a significant contribution to the quasicrystal entropy. Here, we use free-energy calculations to demonstrate that it is this configurational entropy which stabilizes a dodecagonal quasicrystal in a binary mixture of hard spheres on a plane. Our calculations also allow us to quantitatively confirm that in this system all tiling realizations are essentially equally likely, with free-energy differences less than $0.0001k_B T$ per particle—an observation that could be related to the observation of only random tilings in soft-matter quasicrystals. Owing to the simplicity of the model and its available counterparts in colloidal experiments, we believe that this system is an excellent candidate to achieve the long-awaited quasicrystal self-assembly on the micron scale.

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Hard spheres have played a foundational role in our quest to understand classical phase behavior—from helping to understand how purely entropic systems can crystallize, to revealing new insights into the behavior of glassy materials, to nucleation, to melting in 2D, and many more [1]. Their success as a model system stems partly from their inherent simplicity, making them amenable to efficient simulations and analytical theories. Moreover, advances in colloidal particle synthesis have largely made it possible to quantitatively test theoretical and numerical predictions in the lab.

Until recently, quasicrystals were one of the few states of matter inaccessible by this simple model system. Quasicrystals are exotic structures which can display symmetries that are forbidden to periodic crystal phases. While highly controversial when first discovered, their place in material science is now well established, with their formation demonstrated in a growing number of both atomic [2–6] and colloidal [7–13] systems. Toy models that display quasicrystalline behavior have generally been fairly complex—many early models made use of non-additive binary mixtures of Lennard-Jones particles or similar potentials [14–16], or monoatomic systems with oscillatory interaction potentials [17–21]. Recent work has also explored patchy particles [22–25], anisotropic interactions [26,27], and stepwise interactions [28,29]. However, even simple binary (additive or nonadditive) hard-disk systems have been predicted to form quasicrystals in the limit of infinite pressure [30,31].

In colloidal experiments, the most straightforward method for realizing such a mixture of disks is by sedimenting mixtures of colloidal hard spheres onto a flat substrate [32–34]. If the gravitational forces are sufficiently

strong, the resulting binary hard-sphere mixture can be mapped to a nonadditive hard-disk mixture, with a well-defined nonadditivity (see Supplemental Material [35]). Note that in the infinite-pressure limit, it has been shown that this nonadditivity significantly enhances the region where a quasicrystal is expected to be stable [31]. We recently used computer simulations to demonstrate the spontaneous self-assembly of two quasicrystal structures in such systems [41]. Given the simplicity of the hard-sphere model and the fact that it is directly representative of an accessible colloidal model system, this makes hard spheres on a plane an ideal system for studying the physics of quasicrystals.

One major question in the study of quasicrystals is the role of configurational entropy in their stability [42,43]. When systems such as hard spheres form quasicrystals, does this happen because the quasicrystal structure maximizes the freedom of particles to vibrate around their quasicrystalline lattice position? Or are they stabilized by the configurational entropy associated with the large number of possible quasicrystal realizations?

Here, using computer simulations and free-energy calculations, we show that the dodecagonal quasicrystal formed by hard spheres on a plane is stabilized by configurational entropy. In fact, without the configurational entropy the quasicrystal would be metastable with respect to a phase separation of periodic crystals. Instead, the configurational entropy promotes a random-tiling quasicrystal where—for this simple hard-sphere model—all realizations contribute equally to the free energy.

As illustrated in Fig. 1 we consider binary mixtures of hard spheres constrained to lie on a flat substrate. We focus on systems with a size ratio $q = \sigma_S/\sigma_L = 0.46$, where $\sigma_{S(L)}$

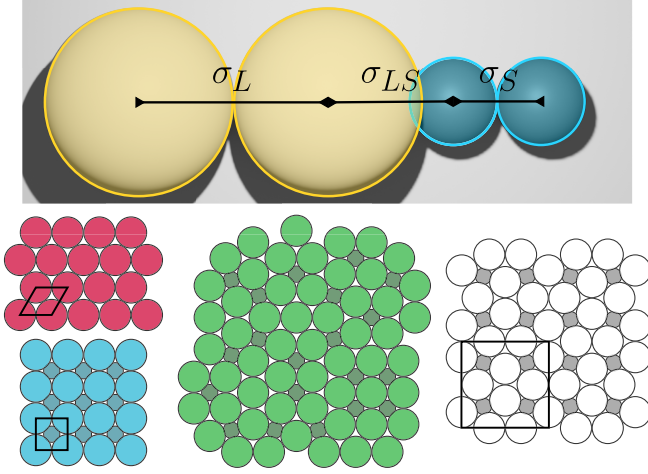


FIG. 1. Top: schematic image of binary hard spheres lying on a flat plane. The line segments indicate the contact distances for the different species. Bottom: candidate phases considered for this system: hexagonal packing (red), S1 (blue), QC12 (green), and Sigma (white). The unit cell of the periodic structures are depicted as black rhombi.

denotes the diameter of the small (large) spheres. Because of the confinement to a flat plane, the particles can move only in two dimensions, and hence in practice we simulate an effective mixture of nonadditive hard disks, where the minimum distance of approach between two disks of unequal size is given by $\sigma_{LS} = \sqrt{\sigma_S \sigma_L}$. Such mixtures are characterized by the composition $x_S = N_S/N$, with $N_{S(L)}$ the number of small (large) spheres and N the total number of spheres. The last free parameter in this model is the packing fraction, which we define as $\eta = (N_S \sigma_S^2 + N_L \sigma_L^2) \pi / 4A$, with A the (two-dimensional) volume of the system.

Previous work showed that a dodecagonal quasicrystal-line phase (QC12) is stable at infinite pressure in this system, and also forms spontaneously in self-assembly simulations [41]. However, this does not prove the thermodynamic stability of this phase, as it could still be metastable with respect to competing periodic crystal phases. Here, we perform free-energy calculations to settle this question, and in particular focus on the role of configurational entropy.

To prove the thermodynamic stability of the QC12 phase, we use explicit free-energy calculations using both event-driven molecular dynamics simulations [44] and Monte Carlo simulations [45]. In particular, we calculate the free energy of different competing phases as a function of the pressure and composition using thermodynamic integration methods [45]. For the fluid phase, we use the ideal gas as a reference state. For the periodic crystal phases, we obtain reference free energies using the Einstein molecule variant [46,47] of the Frenkel-Ladd method [48]. As candidate structures, we consider the phases that are expected to be stable (or nearly stable) at infinite pressure,

namely the hexagonal, S1, Sigma, and QC12 phases [31]. The candidate phases are depicted in Fig. 1. However, our calculations show that the Sigma phase is never favored in comparison to the other phases.

Determining the stability of a quasicrystal using computer simulations presents challenges that are not present for conventional crystal phases. First, quasicrystals are nonperiodic, and hence the finite-size effects of approximating its aperiodic structure with a periodic approximant should be carefully checked. More importantly, quasicrystals are often random tilings, consisting of repeated tiles which can tile space in a multitude of different configurations. The quasicrystals of interest here, like many dodecagonal quasicrystals discovered in soft-matter experiments [8–11] and simulations [7,14,28,29,41,49], are based on a random tiling of the plane by squares and equilateral triangles, with the large particles in the system forming the corners of both shapes. As the number of possible arrangements of these tiles scales exponentially in the number of particles, the freedom of choice in generating this configuration contributes to the total entropy of the phase, and hence needs to be taken into account in any free-energy calculations.

This issue is most easily handled if we can make the assumption that all realizations of the quasicrystal are equally likely, also known as the random tiling hypothesis [50]. If this is the case, the vibrational and configurational entropy are decoupled, and we can split the total free energy of our hard-sphere quasicrystal into two parts:

$$F_{\text{tot}}(N, A, T) = -TS_{\text{vib}}(N, A, T) - TS_{\text{conf}}, \quad (1)$$

where S_{vib} is the vibrational entropy of any given quasicrystal realization, S_{conf} is the configurational entropy associated with the quasicrystal tiling, and T is the temperature. The vibrational entropy can be directly calculated for any given realization using the same Einstein molecule approach as we use for the periodic phases.

The configurational entropy of a lattice-based QC12 square-triangle tiling (without thermal fluctuations) is well studied [51]. When the ratio of the number of squares N_{sq} and triangles N_{tr} reaches $N_{\text{sq}}/N_{\text{tr}} = \sqrt{3}/4$, the random tiling ensemble reaches a maximum entropy, meaning that the number of tilings in the ensemble, or equivalently the number of possible configurations for the squares and triangles, is the highest. At this point, the random tiling ensemble forms a so-called random-tiling quasicrystal of 12-fold symmetry [52–56]. The configurational entropy of the square-triangle tiling was first estimated with transfer matrix [53,57] and numerical [51] approaches, before exact analytical expressions were obtained with a Bethe ansatz [52,54]. Based on these works, the random tiling configurational entropy per particle is given by

$$S_{\text{conf}}/Nk_B = [\ln(108) - 2\sqrt{3}\ln(2 + \sqrt{3})](1 - x_S^{\text{QC12}}) \approx 0.082. \quad (2)$$

Here, x_S is the composition of the system which corresponds to the ratio of squares and triangles required for a quasicrystal, i.e., $x_S^{\text{QC12}} = \sqrt{3}/(2 + 2\sqrt{3}) \approx 0.317$. Importantly, S_{conf} is sharply peaked at this composition, and $-TS_{\text{conf}}$ is nonconvex on either side of the maximum [54], such that random tilings at any compositions other than x_S^{QC12} are strongly entropically disfavored.

In our hard-sphere mixture, it is not *a priori* obvious that all quasicrystal realizations are equally likely. In practice, the probability of finding the system in a given state is proportional to $\propto \exp(-S_{\text{vib}}/k_B)$, and hence we can only use Eq. (2) if all random tiling configurations have essentially the same vibrational entropy. To check this, we perform high-precision calculations of the vibrational entropy of various tiling realizations. In particular, we compare S_{vib} of several types of *ideal* quasicrystal configurations, as well as fully randomized tilings. Ideal quasicrystal configurations can be generated by inflation methods, in which every tile of a tiling is replaced by a cluster of tiles. By iterating the inflation rules on an initial seed, one generates larger and larger patches of tiling that converge to a quasicrystalline configuration. Here we generate a quasicrystal tiling with dodecagonal symmetry via the Schlottmann inflation rule [58,59]. Additionally, we construct a quasicrystal tiling with hexagonal symmetry using the Stampfli inflation rule [60]. A slight variation of the Stampfli rule uses random choices to generate a limited ensemble of random tiling realizations with 12-fold symmetry on average. Finally, configurations from the full random tiling ensemble can be sampled by reshuffling ideal configurations using so-called zipper moves that rearrange tiles along a closed path in the tiling [51]. More details on the generation of our tiling configurations can be found in the Supplemental Material [35]. We calculate the vibrational entropy of configurations from each of these families for several different system sizes. For the random tilings, we consider 5 different realizations for each system size. The density is fixed at $1.5\sigma_{\text{LL}}^2$ for all systems. Note that in order to minimize statistical error and reduce the error bars, we repeat the entropy calculation for each configuration at least 100 times [35] and average over the results.

The results are shown in Fig. 2. The finite-size scaling of the entropy appears to be nonlinear for each structure. Interestingly, adding the heuristic finite-size correction term $-\ln(N)/(2N)$ proposed in Ref. [45] does not remove the nonlinearity. Given the plateaulike behavior in the limit of large system sizes, we simply use the value of the entropy per particle for the largest systems as our estimate of the vibrational entropy in the thermodynamic limit. We obtain $S_{\text{vib}}/Nk_B = -5.50309(5)$ for the Schlottmann quasicrystal, $-5.50317(4)$ for the random Stampfli

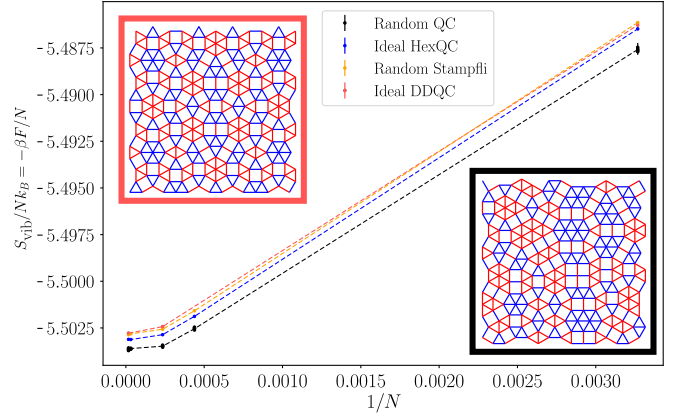


FIG. 2. Vibrational entropies of the Schlottmann dodecagonal quasicrystal (DDQC, pink), random Stampfli quasicrystal (orange), Stampfli hexagonal quasicrystal (HexQC, blue), and 5 fully random quasicrystals (random QC, black), for various system sizes. The error bars are the statistical error on the mean obtained by repeating Frenkel-Ladd calculations many times, and are smaller than the symbols for most points. Two system sizes are obtained by inflation of a sigma seed, for which our implementation of the Schlottmann inflation fails. Hence, two pink points are missing. The insets show examples of an ideal Schlottmann tiling (top left) and a random tiling (bottom right).

quasicrystal, $-5.50342(4)$ for the Stampfli hexagonal quasicrystal, and $-5.50392(4)$ for the average over the 5 largest realizations of the random-tiling quasicrystal.

An important first observation is that the vibrational entropies of the 5 random-tiling quasicrystals are degenerate within our error bars for all system sizes studied (black clusters in Fig. 2). Moreover, even including the rare idealized tilings the vibrational entropies agree to within $0.001k_B$ per particle. This indicates that the configurations in the random tiling ensemble indeed have essentially indistinguishable vibrational entropies. This observation quantitatively validates the assumption that all realizations are equally likely in our system and justifies the treatment of the QC12 as a random tiling phase with the configurational entropy given by Eq. (2).

The measurements show, nonetheless, that some configurations in the random tiling ensemble are special. The entropy of the inflated quasicrystals is consistently larger than that of the random configurations, with the entropy difference on the order of $10^{-3}k_B$ per particle. Interestingly, we find that the ideal dodecagonal quasicrystal obtained with Schlottmann inflation has slightly more vibrational entropy than both the ideal hexagonal Stampfli and random Stampfli quasicrystals. Nonetheless, given that the configurational entropy of the random tiling ensemble [Eq. (2)] is orders of magnitude larger than the small vibrational entropy gain associated with adopting an idealized quasicrystal realization, our results show that the random tiling state is overwhelmingly more stable than any idealized tiling.

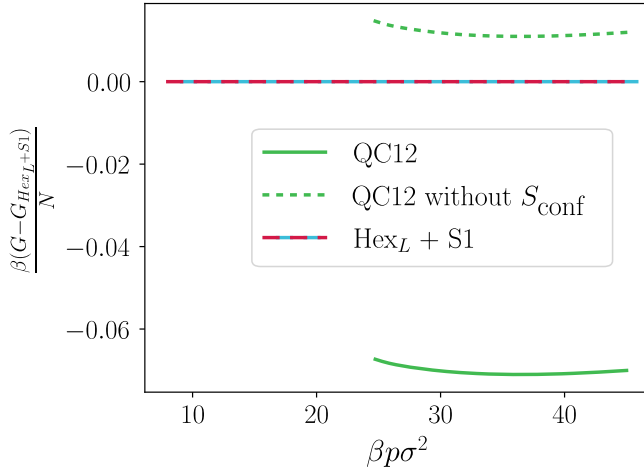


FIG. 3. Free-energy difference between the competing coexistence of $\text{Hex}_L + \text{S1}$ and the quasicrystal at the quasicrystal composition. For the quasicrystal, the dashed curve corresponds to the vibrational entropy alone and lies above the coexistence free energy. The addition of the constant tiling entropy term (solid line) stabilizes the quasicrystal.

The vibrational entropy difference between random and ideal quasicrystals can be understood from the different local environments that can be found in the underlying tiling. For instance, the idealized quasicrystals contain no local environments formed of 4 squares meeting at the same vertex, while the random quasicrystals contain a nonzero concentration of these vertices [61] (see insets in Fig. 2). We expect, however, that the first-neighbor local environments alone do not explain fully the entropy difference. Indeed, both the dodecagonal and hexagonal ideal quasicrystals have the same distribution of local environments when considering only the first-neighbor shell. Hence, neighbor shells beyond the first one certainly play a non-negligible role.

From the point of view of quasicrystal theory, the vibrational entropy difference between ideal and random structures is an interesting illustration of phonon-phason coupling [19,50], albeit very weak. The vibrational entropy of each system can be interpreted as stemming from the total entropy contribution from all phonon modes accessible to the quasicrystal. In this picture, the lower vibrational entropy of the random quasicrystals shows that the presence of phason modes in these systems hinders lattice vibrations, i.e., reduces the amplitude of the phonon modes.

Now that we have verified that we can use Eq. (2) to determine the configurational entropy of the quasicrystal phase, we can determine its stability in comparison to the other crystal phases. To this end, we transform the entropies obtained from our thermodynamic integration into Gibbs free energies using the equation of state of the respective phases, and compare different phases (or coexistences thereof) at the same pressure. In Fig. 3, we plot the Gibbs free energy for the quasicrystal (obtained via Schlottmann inflation) relative to that of the closest

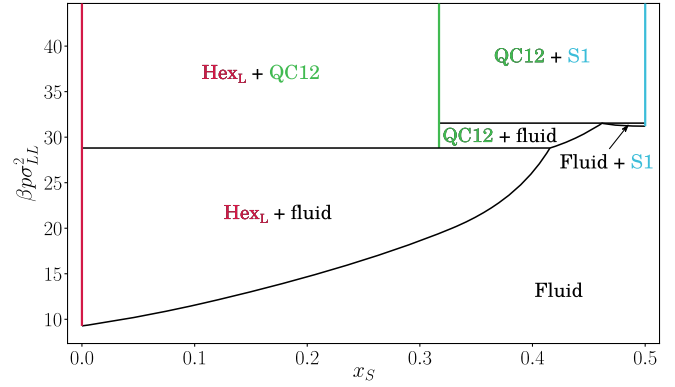


FIG. 4. Phase diagram of binary mixtures of nonadditive hard disks with size ratio $q = 0.46$ corresponding to the equivalent 3D geometry of spheres sedimented on a flat surface. The random tiling dodecagonal quasicrystal is labeled “QC12.” Although considered as a candidate phase, the Sigma approximant of the quasicrystal is nowhere stable.

competing periodic state: a coexistence of the hexagonal Hex_L crystal and square S1 crystal. Without the configurational entropy term (green dashed line), the Hex_L -S1 coexistence prevails and the quasicrystal is not stable. Including the configurational entropy from Eq. (2) results in the solid green line, stabilizing the QC12 phase. Clearly, for this system, the tiling contribution to the total entropy is critical for the quasicrystal stability. Note that the free-energy difference between the QC12 and the coexistence of periodic phases is on the order of $0.07k_B T$, which is more than an order of magnitude larger than the difference between the different families of quasicrystal tilings shown in Fig. 2, and over 2 orders of magnitude larger than the variations in vibrational entropy between individual random tilings.

Finally, we use the free energies we obtained for all different phases to construct the phase diagram of our system as a function of the composition x_S and pressure p . The coexistence regions are mapped out using common tangent constructions at constant pressure. Since the QC12 phase only appears for compositions $x_S < 0.5$, we only consider systems with compositions $x_S \leq 0.5$. As the S1 phase is highly favored for compositions close to $x_S = 0.5$, this allows us to disregard any phases that occur at higher compositions. The resulting phase diagram is shown in Fig. 4, and clearly indicates a broad stable region for the QC12 phase. Additionally, we observe stable regions for the S1, Hex_L , and fluid phases. Note that the Sigma phase is never stable.

Although the QC12 phase coexists with other solid phases for most of its stability range, there is a narrow band of pressures where it coexists with a fluid containing a larger concentration of small particles. As self-assembly is likely to be easier to achieve from a fluid phase, this suggests that self-assembly of this phase may be easiest by starting from an off-stoichiometric fluid with $x_S > x_S^{\text{QC12}}$.

This scenario is in line with earlier self-assembly observations of this phase [41], and has previously been reported for other phases as well [62].

In conclusion, our results demonstrate the thermodynamic stability of a dodecagonal quasicrystal in a binary mixture of hard spheres confined to lie on a flat substrate. As it consists of hard spheres, the quasicrystal considered here is inherently stabilized by entropy alone. Importantly, however, it is also an example of a quasicrystal that is stabilized by its configurational, rather than vibrational, entropy. This configurational entropy stems from the many different possible tiling realizations, which are—as shown by our precise free-energy calculations—nearly indistinguishable in terms of their vibrational freedom. Because of the tiny vibrational entropy difference between different realizations, random tilings are overwhelmingly more likely to form than perfect inflationary tilings.

An intuitive way to understand the minute free-energy differences between different quasicrystal realizations is to consider a cell-theoretical description of the free energy of the quasicrystals. Because of the short-ranged nature of the interactions, in this picture all quasicrystal realizations would have the same free energy, trivially leading to the result that the random-tiling quasicrystal must be stable over any specific realization. As such, we expect our results to hold for other colloidal quasicrystals where the interactions are isotropic and sufficiently short ranged, including, e.g., additive hard disks, steric repulsions, and attractions due to depletion. Interestingly, all the colloidal quasicrystalline systems observed thus far appear to indeed be at least partially random, suggesting a non-negligible contribution of configurational entropy to their stability. Note, however, that in some systems, sufficiently strong particle interactions could favor or suppress different sets of quasicrystal realizations [63], lowering the configurational entropy and potentially destabilizing the quasicrystal phase [19].

The key role played by configurational entropy in the stabilization of the two-dimensional 12-fold quasicrystal studied here is also intriguing when considering self-assembly of three-dimensional structures that consist of stacked layers of 2D quasicrystals [8,10,25]. For systems where consecutive layers correspond to the same tiling, the configurational entropy of such a layered quasicrystal would be proportional to the surface area of a single layer, rather than its volume, as only the first layer formed has the freedom to choose its tiling pattern. As a result, the configurational entropy contribution to the free energy should technically vanish for sufficiently large systems, reducing the thermodynamic stability of random tiling quasicrystals. In practice, however, randomized tilings could still occur if they are “frozen in” during the initial self-assembly of the first layer. Hence, the impact of configurational entropy on the formation of three-dimensional quasicrystals with dodecagonal symmetry remains an open question.

Finally, we note that the geometry of binary hard spheres on a flat surface can be readily realized in experimental systems of colloidal spheres sedimented onto a flat substrate [32–34]. Hence, the prediction of an equilibrium quasicrystal in this system is extremely promising for the creation and study of quasicrystals on the colloidal scale. Such a realization would be an important step forward in the study of (soft-matter) quasicrystals, as it would provide an ideal platform for the real-space study of, e.g., defect dynamics, perpendicular strain relaxation, and other phenomena that are hard to study in molecular or atomic quasicrystals.

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