THERMODYNAMIC LIMIT FOR POLYDISPERSE FLUIDS

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Abstract

We examine the thermodynamic limit of fluids of hard core particles that are polydisperse in size and shape. In addition, particles may interact magnetically. Free energy of such systems is a random variable because it depends on the choice of particles. We prove that the thermodynamic limit exists with probability 1, and is independent of the choice of particles. Our proof applies to polydisperse hard-sphere fluids, colloids and ferrofluids. The existence of a thermodynamic limit implies system shape and size independence of thermodynamic properties of a system.

I. INTRODUCTION

The free energy of a system of particles, as defined in statistical mechanics, depends explicitly on the the size and shape of the container holding the particles (the "system shape") through the dependence of the partition function on these quantities. Thermodynamics, in contrast, assumes a free energy density independent of the system shape and size. For typical systems, as the system size grows the contribution of the boundary to the statistical free energy becomes negligible compared with the bulk contribution. In the thermodynamic limit (system size going to infinity) the free energy density becomes independent of system shape and the boundary conditions.

Ruelle [1] and Fisher [2] proved the existence of thermodynamic limits for a large class of fluids and solids with interactions that fall off faster than r^{-3} at large separation. Interactions which fall off as r^{-3} or slower, complicate the thermodynamic limit. For neutral systems with coulombic interactions, Lieb [3] proved the existence of a thermodynamic limit using the screening of the interaction at large distances. For dipolar interactions, Griffiths [4] proved the existence of a thermodynamic limit for dipolar lattices using magnetization reversal in a domain. The present authors [5] extended Griffiths' proof to several non-lattice models with dipolar interactions.

The systems discussed above contain identical particles with specified interactions. In this paper we study random systems, fluids consisting of hard core particles that are polydisperse in size and shape. A proof of the thermodynamic limit for polydisperse fluids is needed because they occur abundantly in nature and technology, and because their thermodynamic properties are of great interest [6–9].

For a system where the particles are chosen at random from a distribution of size and shape, the free energy is a random variable because it depends on the choice of particles. In general, proof of a thermodynamic limit depends upon the subadditivity of free energy as the system size grows. Thus we must exploit the theory of subadditive random variables [10]. Furthermore, depending on the size and shape distribution of particles, a particular choice of particles may or may not pack into the available volume. Due to these complications, the proof requires a restriction on the particle size and shape distribution in the form of a "packing condition". Thermodynamic limits of random systems have been investigated previously [11–13]. Those results, however, apply only to lattice models.

For our calculations, we fix the choice of particles in a canonical ensemble. Thus, we study "quenched" systems. In contrast, in an "annealed" system the relative concentration of particles of various types are controlled using chemical potentials [8,14]. The quenched and annealed free energies have been studied extensively in the context of spin glass systems [13,15–17]. The quenched free energy is calculated by fixing the interaction between spins whereas the annealed free energy is calculated by averaging the partition function over the random interactions first. The quenched free energy is the desirable quantity since in a real system the interactions are fixed. However, it is often easier to calculate the annealed free energy. It is claimed that for polydisperse fluids the annealed free energy equals the quenched free energy [14].

Polydisperse fluids often phase separate into different liquid or even solid phases with different concentration of particle types in each phase [6–9]. In our terminology quenching fixes the overall concentration of various particle types and not the particle concentration in each phase. This terminology should not be confused with that often used in the literature [9] of polydisperse colloidal systems to describe systems that have reached equilibrium (annealed) in relative particle concentration between the two phases, and systems that have not reached equilibrium (quenched).

In this paper we prove that the free energy density F/V of any random choice of particles goes to some finite limiting value f with probability 1, independent of the choice of particles, as the system size goes to infinity. In Sec. II we carry out the proof for fluids of polydisperse hard core particles. In Sec. III we extend the proof to fluids of hard core particles with magnetic interactions. These systems may be liquids such as ferrofluids [19]. Finally, in Sec. IV we summarize our results and discuss some models that are not covered by our proof.

II. HARD CORE PARTICLES POLYDISPERSE IN SHAPE AND SIZE

In this section we show that, for a fluid of hard core particles polydisperse in size and shape contained within a box of any shape, the free energy density goes to a limit with probability 1 as we take the system size to infinity. Our proof involves three main steps. First, we consider systems of particles contained within cubical containers and show that the free energy density of systems shaped as cubes goes to a limit with probability 1 as the system size goes to infinity. In the second step, we show that this limiting free energy density is independent of the choice of particles. In the the final step, we prove system shape independence of the limit by showing that the limiting free energy density for a system of any arbitrary shape is the same as that of a system shaped as a cube.

In Sec. II A we define our model that includes the particle size and shape distribution, a choice of particles from the distribution, the Hamiltonian, the partition function, and the free energy. We impose an artificial upper bound on the free energy to deal with choices of particles that do not fit inside given containers without overlapping. This section also defines a packing condition on the particle size and shape distribution which guarantees that with high probability the particles fit within containers without overlapping.

In Sec. II B we consider systems shaped as cubes and show that the free energy density satisfies the conditions of a subadditive ergodic theorem [10] so that the free energy density of a cube-shaped system goes to a limit for almost every choice of particles as the cube size goes to infinity. To make use of the subadditive ergodic theorem we define a lattice and divide space into basic cubes defined on the lattice. A choice of particles identifies some specific particles associated with each basic cube. Any box defined on the lattice holds particles assigned to the basic cubes inside the box. The lattice, the basic cubes, and the boxes, are a device for assigning particles to containers in a random but well-defined fashion and employing the subadditive ergodic theorems in the literature.

In Sec. II C we show that the variance of the free energy density around its mean vanishes as the cube size goes to infinity, proving that the limit is in fact independent of the specific choice of particles. In Sec. II D we prove the system shape independence of the free energy density by filling up an arbitrary shaped system with cubes and showing that the free energy density of any arbitrary shape has the same limit as that of a cube.

A. Definitions and assumptions

Let X be a set of particle sizes and shapes (see Fig. 1) with some probability measure μ_1 defined on it. Consider a container S, of volume V_S and a choice $\mathbf{c}_{N_S}$ of N_S hard core particles contained in S, independently chosen from X, one at a time. Denote the set of all such choices by $\mathcal{C}_{N_S}$. The probability measure μ_{N_S} defined on $\mathcal{C}_{N_S}$ is the N_S-fold product of the probability measure μ_1 defined on X. Let $\mathbf{c}$ denote a choice of an infinite sequence of particles and $\mathcal{C}$ denote the set of all possible choices. The probability measure μ defined on $\mathcal{C}$ is the infinite-fold product of μ_1.

The particles can be placed anywhere inside $\mathcal{S}$ with any orientation as long as the Hamiltonian $\mathcal{H}_{\mathcal{S}} = \mathcal{H}_S^{HC}$ is finite, where

$$\mathcal{H}_S^{HC}(\mathbf{c}_{N_S}) = \begin{cases} 0 & \text{if no particles overlap each other or the boundaries of } S \\ +\infty & \text{otherwise,} \end{cases} \tag{1}$$

is the hard core repulsion between the particles. Although not indicated explicitly, $\mathcal{H}_S^{HC}(\mathbf{c}_{N_S})$ depends on the particle center of mass positions $\{\mathbf{r}_i\}$ and the particle orientations $\{\Omega_i\}$. Define the partition function

$$Z_S(\mathbf{c}_{N_S}) = \frac{1}{\Omega^{N_S} N_S!} \int_S \prod_{i=1}^{N_S} d\mathbf{r}_i d\Omega_i e^{-\mathcal{H}_S(\mathbf{c}_{N_S})/k_B T}, \tag{2}$$

where $\Omega = 4\pi$ is the integral of $d\Omega$ over all possible orientations of a particle. The prefactor $N_S!$ is chosen to make the free energy extensive. This factor may be modified depending on the details of the set X to account for the entropy of mixing (see appendix A). However, the factor $N_S!$ suffices as long as we do not "unmix" the particles [6,24].

Because the particle sizes and shapes are drawn at random, sometimes a choice of particles may not fit into the box S without overlapping. Some choices that fit into S may have insufficient room to move. Such choices have large, physically unrealistic, free energies. We wish to remove these unphysical choices from consideration. However, their exclusion causes mathematical inconvenience, since the probability measure for choices would no longer be the product of the single particle probability measure on X. On the other hand, including such choices causes the partition function to vanish for some $\mathbf{c}_{N_S} \in \mathcal{C}_{N_S}$, leading to infinite free energies.

To handle these difficulties, we define an arbitrary threshold $z_0^{N_S}$, for the partition function of a container $\mathcal{S}$. The constant $z_0 > 0$ can be interpreted as a (geometric) mean free phase space volume per particle. We define the free energy in the following artificial manner,

$$F_S(\mathbf{c}_{N_S}) = \begin{cases} -N_S k_B \mathrm{T} \ln z_0 & \text{if } Z_S(\mathbf{c}_{N_S}) < z_0^{N_S} \\ -k_B \mathrm{T} \ln Z_S(\mathbf{c}_{N_S}) & \text{otherwise.} \end{cases} \tag{3}$$

Provided that the particle size and shape distribution X obeys the packing condition discussed below, choices with $Z_S(\mathbf{c}_{N_S}) < z_0^{N_S}$ occur sufficiently infrequently that the limiting free energy density is independent of the arbitrary constant z_0 (see Sec. II C).

Consider a cube Γ of volume V_Γ containing N_Γ particles such that $\rho_\Gamma = N_\Gamma/V_\Gamma$. Let P_Γ be the set of choices $\mathbf{c}_{N_\Gamma} \in \mathcal{C}_{N_\Gamma}$ for which $Z_{\Gamma_\Gamma}(\mathbf{c}_{N_\Gamma}) \geq z_0^{N_\Gamma}$, where N_Γ is the number of particles contained in Γ. Formally,

$$P_\Gamma \equiv \left\{ \mathbf{c}_{N_\Gamma} \in \mathcal{C}_{N_\Gamma} \mid Z_\Gamma(\mathbf{c}_{N_\Gamma}) \geq z_0^{N_\Gamma} \right\} \tag{4}$$

is the set of choices that "pack" in Γ. Let $\{\Gamma\}$ be a sequence of cubes. Our packing condition on the particle size and shape distribution X requires that for any $z_0 > 0$ there exists a "critical packing density" $\rho^*(z_0) > 0$, such that for any density $\rho_\Gamma \leq \rho < \rho^*$,

$$\lim_{V_\Gamma \to \infty} \mu_{N_\Gamma}(P_\Gamma) = 1. \tag{5}$$

Here μ_{N_Γ} is the probability measure associated with the sample space $\mathcal{C}_{N_\Gamma}$. See appendix A for examples of some particle size and shape distributions that satisfy the packing condition.

B. Thermodynamic limit for rectangular and cubical boxes

In this section we show that the free energy density of rectangular boxes goes to a limit with probability 1 (i.e. for almost every $\mathbf{c} \in \mathcal{C}$) as the system size goes to infinity. We assume that the particle distribution X obeys the packing condition Eq. (5) and that the particle density $\rho < \rho^*$. For the proof we make use of a subadditive ergodic theorem (theorem 2.7 in Ref. [10]) by Akcoglu and Krengel.

Consider a tiling of non-negative real space $\mathbb{R}^3_+$ by "basic" cubes with each side of length l_0. The vertices of the basic cubes define a lattice $\mathcal{L}$ such that any point in $\mathcal{L}$ can be written as $(n_1, n_2, n_3)l_0$, where $n_i \in \mathbb{Z}_+$ (nonnegative integers). For vectors $a = (a_i)$ and $b = (b_i)$ in

$\mathcal{L}$, the half-open interval $[a, b)$ denotes the set $\{u | u = (u_i) \in \mathcal{L}, a_i \leq u_i < b_i\}$. Physically, it represents a rectangular box in $\mathbb{R}^3_+$. We call a the "base" of the box. Let $\mathcal{I}$ be the class of all such rectangular boxes. Denote the cube $[w, w + 2^k d)$ by Γ^w_k, where w is any vector in $\mathcal{L}$, d is the vector (l_0, l_0, l_0) and k is any nonnegative integer. Any box $I \in \mathcal{I}$ can be completely filled with the "basic" cubes Γ^w_0, where w runs over the intersection of $\mathcal{L}$ with I.

Let $\mathbf{c}$ be a choice (infinite sequence) of particles. Break up $\mathbf{c}$ into successive sequences of N_0 particles and put one such sequence into each basic cube Γ^w_0 using a one-to-one map from a one-dimensional rectangular array (of sequences of particles) to a three dimensional rectangular array (of basic cubes). Denote the segment of particles in Γ^w_0 by $\mathbf{c}^w_{N_0}$. For any vector $u \in \mathcal{L}$, define a transformation τ_u on $\mathcal{C}$ such that $\mathbf{c}' = \tau_u(\mathbf{c})$ is another choice in $\mathcal{C}$ with ${\mathbf{c}^w_{N_0}}' = \mathbf{c}^{w+u}_{N_0}$ for every $w \in S$. Since μ is a product measure, τ_u is a measure preserving transformation on $\mathcal{C}$.

Consider a rectangular box $I \in \mathcal{I}$, of volume V_I. Let the choice of particles assigned to I be the union of choices $\mathbf{c}^w_{N_0}$ assigned to basic cubes Γ^w_0 contained in I (see Fig. 2). The number of particles in I is $N_I = N_0 V_I / V_{\Gamma_0}$. The subadditive ergodic theorem requires that for each choice $\mathbf{c} \in \mathcal{C}$ the free energy F_I satisfies the following three conditions:

(i) **Translation invariance**: For every box $I \in \mathcal{I}$ and every vector $u \in \mathcal{L}$

$$F_I \circ \tau_u = F_{I+u}. \tag{6}$$

(ii) **Subadditivity**: For any box $I \in \mathcal{I}$ composed of nonoverlapping boxes $I_1, ..., I_n \in \mathcal{I}$

$$F_I \leq \sum_{i=1}^{n} F_{I_i}. \tag{7}$$

(iii) **Lower bound**: For some constant ω_A and for all $I \in \mathcal{I}$

$$\frac{1}{V_I} F_I \geq \omega_A, \tag{8}$$

where V_I is the volume of box I.

Then, the theorem states that for a *sufficiently regular* sequence of rectangular boxes $\{I_k\}$, of increasing size, the free energy density F_{I_k}/V_{I_k} goes to a limit $f(\mathbf{c})$ almost everywhere in

$\mathcal{C}$ as $k \to \infty$. Note that this limit may depend on the choice of the particles $\mathbf{c}$. A sequence of rectangular boxes $\{I_k\}$ of increasing size is sufficiently regular (as defined by Akcoglu and Krengel [10]) if there exists another sequence of rectangular boxes $\{I'_k\}$ such that box I'_k fully covers the box I_k, the ratio $V_{I_k}/V_{I'_k}$ is always greater than or equal to some fixed nonzero constant, and $\lim_{k\to\infty} I'_k = \mathbb{R}^3_+$.

From our definition of the transformation τ_u, the free energy trivially satisfies (6). For any box $I \in \mathcal{I}$ composed of nonoverlapping boxes $I_i \in \mathcal{I}$, the partition functions satisfy

$$Z_I \geq \prod_i Z_{I_i}, \tag{9}$$

because each particle has more room to move inside I than an individual box I_i (see Ref. [2] for the detailed argument). The free energy therefore satisfies subadditivity (7). The free energy also satisfies the lower bound (8) with $\omega_A = k_B \mathrm{T} \rho \ln(\rho)$ which is temperature times the ideal gas entropy per particle.

Hence, the free energy satisfies all the conditions of Akcoglu and Krengel's subadditive ergodic theorem. To apply this to the special case of a cube, construct a sequence of cubes of increasing size $\{\Gamma_k\}$ such that $V_{\Gamma_k} \to \infty$ as $k \to \infty$ and the distance of the bases of the cubes from the origin grows less rapidly than their size. This ensures that the sequence is sufficiently regular in the sense of Akcoglu and Krengel [10]. Then, according to the theorem the free energy density $f_{\Gamma_k} \equiv F_{\Gamma_k}/V_{\Gamma_k}$ goes to some limit $f_\Gamma(\mathbf{c})$, the free energy density in a cube, for almost every $\mathbf{c} \in \mathcal{C}$.

It is interesting to note that the sequence of cubes $\{\Gamma_k\}$ can be chosen so that no cubes overlap with each other and thus have no particles in common. This suggests that the limiting free energy density $f_\Gamma(\mathbf{c})$ should not depend on $\mathbf{c}$. We demonstrate that fact in the following section.

C. Choice independence of the limiting free energy density

In this section we prove that the limiting free energy density $f_\Gamma(\mathbf{c})$ is independent of the choice of particles $\mathbf{c}$. We show that the free energy density averaged over all choices goes to a limit and its variance goes to zero as the cube size goes to infinity. This implies that the limit is same for any choice with probability 1. Furthermore, the limiting value and its variance are independent of z_0, the arbitrary constant introduced in defining free energy.

Let $\langle f_{\Gamma_k} \rangle$ denote the free energy density of a cube Γ_k averaged over all choices $\mathbf{c}_{N_k} \in \mathcal{C}_{N_k}$ of N_k particles in Γ_k. From subadditivity (7) of the free energy it follows that

$$\langle f_{\Gamma_{k+1}} \rangle \leq \langle f_{\Gamma_k} \rangle. \tag{10}$$

The sequence of average free energy densities $\{\langle f_{\Gamma_k} \rangle\}$ is monotonically decreasing and has a lower bound (8). The average free energy density therefore goes to some limit $\bar{f}_\Gamma$ as $k \to \infty$.

To show that the variance of the free energy density of cubes vanishes as the cube size goes to infinity, we construct a cube Γ_{k+1} by putting together eight nonoverlapping cubes Γ_k. By using subadditivity (7), the lower bound (8) and the existence of a limiting average free energy density for cubes we show (see appendix B) that for any $\epsilon > 0$ there exists a sufficiently large k_0 such that for any $k > k_0$,

$$\left\langle \left(f_{\Gamma_{k+1}} - \langle f_{\Gamma_{k+1}} \rangle \right)^2 \right\rangle \leq \frac{1}{8} \left\langle \left(f_{\Gamma_k} - \langle f_{\Gamma_k} \rangle \right)^2 \right\rangle + \epsilon. \tag{11}$$

Iterating this procedure n times we write

$$\left\langle \left(f_{\Gamma_{k+n}} - \langle f_{\Gamma_{k+n}} \rangle \right)^2 \right\rangle \leq \frac{1}{8^n} \left\langle \left(f_{\Gamma_k} - \langle f_{\Gamma_k} \rangle \right)^2 \right\rangle + \sum_{j=0}^{n-1} \frac{1}{8^j} \epsilon. \tag{12}$$

For a fixed value of k there exists n_0 such that, for all $n > n_0$, the first term on the right hand side in the inequality is less than ϵ. The second term on the right hand side approaches $(8/7)\epsilon$ from below. Hence, for any given ϵ, there exist k_0 and n_0 so that for any $k > k_0$ and $n > n_0$, the variance in the free energy density satisfies the upper bound

$$\left\langle \left(f_{\Gamma_{k+n}} - \langle f_{\Gamma_{k+n}} \rangle \right)^2 \right\rangle \leq \frac{15}{7} \epsilon. \tag{13}$$

For a sufficiently large system the variance of the free energy density becomes arbitrarily small. We previously proved (Sec. II B) that f_{Γ_k} goes to a limit $f_\Gamma(\mathbf{c})$ for almost every choice $\mathbf{c}$ of particles. A vanishing variance implies (by using Chebyshev's inequality [18]) that the probability of $f_\Gamma(\mathbf{c})$ differing from $\bar{f}_\Gamma$ by more than some arbitrarily small fixed amount, also vanishes. The values of $f_\Gamma(\mathbf{c})$ thus converge "in probability" to $\bar{f}_\Gamma$. The existence of the limit $f_\Gamma(\mathbf{c})$ with probability 1 together with convergence in probability to $\bar{f}_\Gamma$ implies that $f_\Gamma(\mathbf{c})$ equals $\bar{f}_\Gamma$ with probability 1. In appendix C we show that $\bar{f}_\Gamma$ is a convex and continuous function of the density ρ.

Finally, we show that the limit $\bar{f}_\Gamma$ and the variance are independent of the arbitrary constant z_0. Let P_{Γ_k} be the set of choices that pack in a cube Γ_k as defined in Sec. II A. Let Q_{Γ_k} be the complement of P_{Γ_k} so that $\mu_{N_k}(P_{\Gamma_k}) + \mu_{N_k}(Q_{\Gamma_k}) = 1$. Write the free energy density for a cube Γ_k averaged over all choices as

$$\bar{f}_{\Gamma_k} = \int_{P_{\Gamma_k}} d\mu_{N_k}\; f_{\Gamma_k} + \int_{Q_{\Gamma_k}} d\mu_{N_k}\; f_{\Gamma_k}. \tag{14}$$

From the definition of free energy (3) it follows that

$$\bar{f}_{\Gamma_k} = \int_{P_{\Gamma_k}} d\mu_{N_k}\; f_{\Gamma_k} \;-\; k_B \mathrm{T} \ln z_0 \;\mu_{N_k}(Q_{\Gamma_k}). \tag{15}$$

By the packing condition, $\mu_{N_k}(P_{\Gamma_k}) \to 1$ and $\mu_{N_k}(Q_{\Gamma_k}) \to 0$, as $k \to \infty$. Hence $\bar{f}_\Gamma$ is independent of z_0. Now write the variance of the free energy density as

$$\langle (f_{\Gamma_k} - \bar{f}_{\Gamma_k})^2 \rangle = \int_{P_{\Gamma_k}} d\mu_{N_k}\; (f_{\Gamma_k} - \bar{f}_{\Gamma_k})^2 + \int_{Q_{\Gamma_k}} d\mu_{N_k}\; (f_{\Gamma_k} - \bar{f}_{\Gamma_k})^2. \tag{16}$$

From the definition of free energy (3) it follows that

$$\langle (f_{\Gamma_k} - \bar{f}_{\Gamma_k})^2 \rangle = \int_{P_{\Gamma_k}} d\mu_{N_k}\; (f_{\Gamma_k} - \bar{f}_{\Gamma_k})^2 + (k_B \mathrm{T} \ln z_0 + \bar{f}_{\Gamma_k})^2 \;\mu_{N_k}(Q_{\Gamma_k}). \tag{17}$$

Since $\mu_{N_k}(Q_{\Gamma_k}) \to 0$ as $k \to \infty$, because of the packing condition (5), the contribution of the choices $\mathbf{c}_{N_k} \in Q_{\Gamma_k}$ to the variance vanishes. Hence the variance is independent of z_0. We can then remove the free energy threshold in Eq. (3) by taking the limit of $z_0 \to 0$.

D. System shape independence of the limiting free energy density

Now we prove that for a sufficiently regular (in the sense of Fisher [2]) sequence of shapes $\{S_j\}$, the free energy density goes to a limit as $V_{S_j} \to \infty$, provided that the density of particles $\rho = N_{S_j}/V_{S_j}$ remains fixed. Note that the volumes V_{S_j} must be adjusted so that N_{S_j} is an integer. To prove shape independence we show that the limiting free energy density satisfies the bounds

$$\lim_{j\to\infty} \sup f_{S_j} \leq \bar{f}_\Gamma \tag{18}$$

and

$$\lim_{j\to\infty} \inf f_{S_j} \geq \bar{f}_\Gamma \tag{19}$$

with probability 1. To show these bounds we use a technique similar to that of Fisher in his proof for identical particles.

Consider a maximal filling of the shape S_j by n_{jk} cubes Γ_k^w so that each of the cubes Γ_k^w is fully contained within S_j (see Fig. 3). The length l_0 of the side of the basic cubes Γ_0 is chosen such that there exists an integer N_0 such that $N_0/l_0^3 = \rho$. This ensures that it is possible to achieve density ρ in Γ_k^w exactly. The total number of particles in S_j must equal $N_{S_j} = \rho V_{S_j}$. Therefore, in general, not all n_{jk} cubes contain equal numbers of particles. Let there be two types of cubes, A and B, such that type A cubes contain $N_{jk} = [N_{S_j}/n_{jk}]$ particles and type B cubes contain $N_{jk}+1$ particles independently chosen from the particle distribution X. Here $[y]$ denotes the greatest integer less than or equal to y. Note that because of our choice of l_0, N_{jk} must equal $2^k N_0$ plus some nonnegative integer. To ensure that the number of particles in S_j is N_{S_j}, the numbers of type A and type B cubes (respectively n_{jk}^A and n_{jk}^B), obey

$$N_{S_j} = n_{jk}^A N_{jk} + n_{jk}^B (N_{jk}+1) \tag{20}$$

and $n_{jk} = n_{jk}^A + n_{jk}^B$.

Let $\rho_{jk}^A = N_{jk}/V_{\Gamma_k}$ and $\rho_{jk}^B = (N_{jk}+1)/V_{\Gamma_k}$ be the density of particles in cubes of type A and B respectively, and $\phi_{jk}^A = n_{jk}^A/n_{jk}$ and $\phi_{jk}^B = n_{jk}^B/n_{jk}$ be the fractions of cubes of type A and B respectively. Define $n_{jk}V_{\Gamma_k}/V_{S_j} = 1-\zeta_{jk}$, so that ζ_{jk} is the fraction of volume in S_j unfilled by the cubes Γ_k^w. The density ρ of particles in S_j is related to the densities of particles in the cubes by

$$\rho = (1 - \zeta_{jk})(\phi^A_{jk}\rho^A_{jk} + \phi^B_{jk}\rho^B_{jk}). \tag{21}$$

The density ρ^A_{jk} must always be greater than or equal to ρ because if $\rho^A_{jk} < \rho$, then $\rho^B_{jk} \leq \rho$ (since type B cubes have only one more particle than type A cubes), and Eq. (21) cannot be satisfied for $\zeta_{jk} > 0$. In the event that $\zeta_{jk} = 0$ we have $\phi^A_{jk} = 1$ and the equality $\rho^A_{jk} = \rho$ holds.

Let $\mathbf{c}$ be a choice (infinite sequence) of particles. Put the first N_{S_j} particles of the sequence into S_j and denote them by $\mathbf{c}_{S_j}$. Split $\mathbf{c}_{S_j}$ into n^A_{jk} successive sequences of N_{jk} particles followed by n^B_{jk} successive sequences of $N_{jk}+1$ particles. Label these sequences as $\mathbf{c}^w_{N_{jk}}$ and $\mathbf{c}^w_{N_{jk}+1}$ (depending on their length) using a map from the one-dimensional array (of sequences of particles) to a three-dimensional array (of cubes Γ^w_k). Put particles sequences labeled by superscript w into cube Γ^w_k. From the subadditivity of free energy it follows that

$$F_{S_j}(\rho, \mathbf{c}_{S_j}) \leq \sum_{w\in A} F_{\Gamma^w_k}(\rho^A_{jk}, \mathbf{c}^w_{N_{jk}}) + \sum_{w\in B} F_{\Gamma^w_k}(\rho^B_{jk}, \mathbf{c}^w_{N_{jk}+1}), \tag{22}$$

where the sum over $w \in A$ and $w \in B$ includes all cubes Γ^w_k of type A and type B respectively. We include the density as an argument for free energy and free energy density for the sake of clarity where two or more different densities are present in the same equation. The density is assumed to be ρ if not indicated explicitly. The free energy densities satisfy

$$f_{S_j}(\rho, \mathbf{c}_{S_j})\ V_{S_j} \leq V_{\Gamma_k}\Big\{\sum_{w\in A} f_{\Gamma^w_k}(\rho^A_{jk}, \mathbf{c}^w_{N_{jk}}) + \sum_{w\in B} f_{\Gamma^w_k}(\rho^B_{jk}, \mathbf{c}^w_{N_{jk}+1})\Big\}. \tag{23}$$

Rearranging terms we get

$$f_{S_j}(\rho, \mathbf{c}_{S_j}) \leq (1-\zeta_{jk})\Big\{\frac{\phi^A_{jk}}{n^A_{jk}}\sum_{w\in A} f_{\Gamma^w_k}(\rho^A_{jk}, \mathbf{c}^w_{N_{jk}}) + \frac{\phi^B_{jk}}{n^B_{jk}}\sum_{w\in B} f_{\Gamma^w_k}(\rho^B_{jk}, \mathbf{c}^w_{N_{jk}+1})\Big\}. \tag{24}$$

If $n^B_{jk} = 0$, then the sum over type B cubes on the right hand side is not present because there are no type B cubes.

Take the limit $j \to \infty$, holding k fixed. For sufficiently regular shapes (as defined by Fisher [2]) $\zeta_{jk} \to 0$. Since $\rho^A_{jk} \geq \rho$ can only take discrete values, it follows from Eq. (21) that there exists j_0, such that for all $j \geq j_0$

$$\rho^A_{jk} = \rho. \tag{25}$$

Therefore, $\phi^A_{jk} \to 1$ and $\phi^B_{jk} \to 0$ as $j \to \infty$.

The free energies $f_{\Gamma^w_k}(\rho)$ are identically distributed, independent random variables, because the cubes Γ^w_k are identical in shape and the particles are independently chosen. By the Strong Law of Large Numbers [18]

$$\lim_{j\to\infty} \frac{1}{n^A_{jk}} \sum_{w\in A} f_{\Gamma^w_k} \to \langle f_{\Gamma_k} \rangle \tag{26}$$

with probability 1 . Therefore, the limit of Eq. (24) becomes

$$\lim_{j\to\infty} \sup\, f_{S_j} \le \langle f_{\Gamma_k} \rangle \tag{27}$$

with probability 1. Now take the limit $k \to \infty$ to get the desired upper bound (18) with probability 1.

To show the lower bound on the limiting free energy (19) enclose the shape S_j completely inside the smallest possible cube Γ_K whose edge length is an integer multiple of $2^k l_0$ (see Fig 3). Fill the empty space between S_j and Γ_K with n_{jk} cubes Γ^w_k which lie completely outside S_j. Fix the density of particles in Γ_K at ρ by using two types of cubes Γ^w_k, type A cubes that contain $N_{jk} = [\rho(V_{\Gamma_K} - V_{S_j})/n_{jk}]$ particles and type B cubes that contain $N^B_{jk} = N_{jk} + 1$ particles.

The number of particles in Γ_K,

$$N_{\Gamma_K} = N_{S_j} + n^A_{jk} N_{jk} + n^B_{jk}(N_{jk} + 1), \tag{28}$$

where n^A_{jk} and n^B_{jk} are the number of type A and type B cubes respectively. Dividing by V_{Γ_K} on both sides gives

$$\rho = \frac{V_{S_j}}{V_{\Gamma_K}} \rho + \Big(\frac{n_{jk} V_{\Gamma_k}}{V_{\Gamma_K}}\Big)(\phi^A_{jk}\rho^A_{jk} + \phi^B_{jk}\rho^B_{jk}). \tag{29}$$

We rewrite this relation, introducing $\Phi_j \equiv V_{S_j}/V_{\Gamma_K} \le 1$, and introducing $\zeta_{jk} \ge 0$ as the ratio of volume that is unfilled by the cubes Γ^w_k to that of S_j. Formally, $(V_{\Gamma_K} - n_{jk} V_{\Gamma_k})/V_{S_j} = 1 + \zeta_{jk}$. Then eq. (29) becomes

$$\rho(1-\Phi_j) = (1-\Phi_j(1+\zeta_{jk}))(\phi_{jk}^A\rho_{jk}^A + \phi_{jk}^B\rho_{jk}^B). \tag{30}$$

It follows from Eq. (30) that $\rho_{jk}^A \geq \rho$, because if $\rho_{jk}^A < \rho$ then $\rho_{jk}^B \leq \rho$ and Eq. (30) cannot be satisfied for $\zeta_{jk} > 0$. In the event that $\zeta_{jk} = 0$ then $\phi_{jk}^A = 1$ and $\rho_{jk}^A = \rho$.

Let $\mathbf{c}$ be a choice (infinite sequence) of particles. Denote the first N_{Γ_K} particles of $\mathbf{c}$ by $\mathbf{c}_{\Gamma_K}$. Split $\mathbf{c}_{\Gamma_K}$ into a subsequence of N_{S_j} particles followed by n_{jk}^A successive subsequences of N_{jk} particles and n_{jk}^B successive subsequences of $N_{jk}+1$ particles. Denote the subsequence of N_{S_j} particles by $\mathbf{c}_{S_j}$, and subsequences of N_{jk} and $N_{jk}+1$ particles by $\mathbf{c}_{N_{jk}}^w$ and $\mathbf{c}_{N_{jk}+1}^w$ respectively, using a map from the one-dimensional array (of sequences of particles) to a three-dimensional array (of cubes Γ_k^w). Put particles denoted by $\mathbf{c}_{S_j}$ into S_j and particles labeled by superscripts w into cubes Γ_k^w. From the subadditivity of free energy it follows that

$$F_{\Gamma_K}(\rho, \mathbf{c}_{\Gamma_K}) \leq F_{S_j}(\rho, \mathbf{c}_{S_j}) + \sum_{w\in A} F_{\Gamma_k^w}(\rho_{jk}^A, \mathbf{c}_{N_{jk}}^w) + \sum_{w\in B} F_{\Gamma_k^w}(\rho_{jk}^B, \mathbf{c}_{N_{jk}+1}^w), \tag{31}$$

Rewriting the above in terms of free energy densities and isolating f_{S_j} gives

$$f_{S_j}(\rho, \mathbf{c}_{S_j}) \geq \frac{V_{\Gamma_K}}{V_{S_j}} f_{\Gamma_K}(\rho, \mathbf{c}_{\Gamma_K}) - \frac{V_{\Gamma_k}}{V_{S_j}}\Big\{\sum_{w\in A} f_{\Gamma_k^w}(\rho_{jk}^A, \mathbf{c}_{N_{jk}}^w) + \sum_{w\in B} f_{\Gamma_k^w}(\rho_{jk}^B, \mathbf{c}_{N_{jk}+1}^w)\Big\}. \tag{32}$$

Rearranging terms further, write

$$\begin{aligned} f_{S_j}(\rho, \mathbf{c}_{S_j}) \geq{}& (1+\zeta_{jk})\Big\{\frac{\phi_{jk}^A}{n_{jk}^A}\sum_{w\in A} f_{\Gamma_k^w}(\rho_{jk}^A, \mathbf{c}_{N_{jk}}^w) + \frac{\phi_{jk}^B}{n_{jk}^B}\sum_{w\in B} f_{\Gamma_k^w}(\rho_{jk}^B, \mathbf{c}_{N_{jk}+1}^w)\Big\} \\ &+ \frac{V_{\Gamma_K}}{V_{S_j}}\Big\{f_{\Gamma_K}(\rho, \mathbf{c}_{\Gamma_K}) - \Big(\frac{\phi_{jk}^A}{n_{jk}^A}\sum_{w\in A} f_{\Gamma_k^w}(\rho_{jk}^A, \mathbf{c}_{N_{jk}}^w) + \frac{\phi_{jk}^B}{n_{jk}^B}\sum_{w\in B} f_{\Gamma_k^w}(\rho_{jk}^B, \mathbf{c}_{N_{jk}+1}^w)\Big)\Big\}. \end{aligned} \tag{33}$$

Take the limit $j \to \infty$ so that $\zeta_{jk} \to 0$. Since $\rho_{jk}^A \geq \rho$ is discrete, it follows from Eq. (30) that there exists j_0 such that $\rho_{jk}^A = \rho$ for $j \geq j_0$. Therefore, $\phi_{jk}^A \to 1$ and $\phi_{jk}^B \to 0$ as $j \to \infty$. For the sequence $\{S_j\}$ of sufficiently regular shapes [2], $(V_{\Gamma_K}/V_{S_j}) \geq \delta_S$ for some $\delta_S > 0$. Using the Strong Law of Large Numbers [18] we get that the inequality

$$\lim_{j\to\infty}\inf\, f_{S_j} \geq \langle f_{\Gamma_k}\rangle - \delta_S|f_\Gamma - \langle f_{\Gamma_k}\rangle| \tag{34}$$

is satisfied with probability 1. Now take the limit $k \to \infty$ so that $\langle f_{\Gamma_k}\rangle \to \bar{f}_\Gamma$. Therefore, the lower bound (19) is satisfied with probability 1.

Combining the two bounds (18) and (19) we get

$$\lim_{j\to\infty} f_{S_j} = \bar{f}_\Gamma \tag{35}$$

with probability 1. Therefore, the limiting free energy density f exists with probability 1 for any shape and is independent of the shape of the system. Its value is equal to $\bar{f}_\Gamma$.

III. HARD CORE MAGNETIC PARTICLES POLYDISPERSE IN SIZE AND SHAPE

In this section we extend our proof to fluids which consist of polydisperse hard core particles, as in Sec. II, but in addition, they interact magnetically with each other. One example of such a system is a ferrofluid [19], which is a colloidal suspension of ferromagnetic particles in a carrier liquid. The thermodynamic limit in this case is complicated by the $1/r^3$ fall-off of the magnetic interaction where the exponent of $1/r$ exactly matches the dimensionality of space.

We prove the existence of a thermodynamic limit with probability 1 for fluids of magnetic hard core particles using a strategy similar to that of hard core particles in Sec. II. We show that the free energy satisfies translation invariance (6), subadditivity (7), and the lower bound (8). Once these relations are established, the rest of the proof of a thermodynamic limit is identical to that of the hard core particles in Sec. II and is omitted to avoid repetition.

A. Definitions and assumptions

Let the particles be chosen from a distribution of size, shape and magnetization, X. The magnetization is uniform inside each particle and has a definite relation to the orientation of the particle. The magnitude of the magnetization is the same for all particles. We consider both superparamagnetic particles where the magnetization $\mathbf{M}_i$ can reverse independently of the particle orientation [20,21] Ω_i, and non-superparamagnetic particles with magnetization fixed relative to particle orientation. For the non-superparamagnetic particles, we require that the particle shape have a two-fold rotation symmetry about any axis perpendicular to its magnetization (see Fig. 4) [5].

Consider a container S and a choice of particles $\mathbf{c}_{N_S}$. The magnetic interaction between any two non-overlapping particles i, j inside S is

$$U_S^{ij} = \int_{v_i} d^3\mathbf{r} \int_{v_j} d^3\mathbf{r}' \Big\{ \frac{\mathbf{M}_i(\mathbf{r}) \cdot \mathbf{M}_j(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|^3} - \frac{3(\mathbf{M}_i(\mathbf{r}) \cdot (\mathbf{r}-\mathbf{r}'))\ (\mathbf{M}_j(\mathbf{r}') \cdot (\mathbf{r}-\mathbf{r}'))}{|\mathbf{r}-\mathbf{r}'|^5} \Big\}, \tag{36}$$

where v_i and v_j are the regions of space occupied by the magnetic material of particle i and j, and $\mathbf{M}_i(\mathbf{r})$ is $\mathbf{M}_i$ for $\mathbf{r}$ inside v_i and zero outside. Write the Hamiltonian as

$$\mathcal{H}_S(\mathbf{c}_{N_S}) = \begin{cases} \mathcal{H}_S^M & \text{if no particles overlap each other or the boundaries of } S \\ +\infty & \text{otherwise,} \end{cases} \tag{37}$$

where

$$\mathcal{H}_S^M = \sum_{i<j=1}^{N} U_S^{ij} \tag{38}$$

is the magnetic interaction between the particles. Define the partition function Z_S for the box in the same manner as in (2). For superparamagnetic particles where the magnetization can rotate relative to the particle orientations, we include in Ω_i, in addition to the Euler angles, a discrete variable $O_i = \pm 1$ specifying that the magnetization is parallel $(+1)$ or opposite (-1) to a direction fixed in the particle, and $\int d\Omega_i$ includes a sum over O_i. We may permit magnetization to rotate independently of the particle orientation by augmenting the integration in (2) with an integration over the direction of $\mathbf{M}$. We require that the particle distribution satisfy the packing condition (5) and define the free energy F_S as in (3). The free energy, which depends on the choice of particles, trivially satisfies the translation invariance (6).

B. Subadditivity of the free energy

To show that the free energy satisfies subadditivity (7), we consider a container S composed of two adjacent nonoverlapping rectangular boxes $I_1, I_2 \in \mathcal{I}$. Define the interaction energy between the two boxes I_1, I_2 by

$$\mathcal{H}_{I_1,I_2} \equiv \mathcal{H}_S - \mathcal{H}_{I_1} - \mathcal{H}_{I_2} \tag{39}$$

Let $F_S(\lambda)$ be the free energy of the combined system when the Hamiltonian is $\mathcal{H}_{I_1} + \mathcal{H}_{I_2}$ plus a scaled interaction $\lambda\mathcal{H}_{I_1,I_2}$. Because $F_S(\lambda)$ is a concave function (that is, $F_S''(\lambda) \leq 0$), it is bounded above by

$$F_S(\lambda) \leq F_S(0) + \lambda F_S'(0), \tag{40}$$

where the right side is a line tangent to the graph of $F_S(\lambda)$ at $\lambda = 0$; here $F_S'(\lambda)$ and $F_S''(\lambda)$ are the first and second derivatives.

As a consequence of (40), the free energy $F_S(1)$ of the fully interacting system satisfies the Gibbs inequality [22]

$$F_S(1) \leq F_S(0) + [\mathcal{H}_{I_1,I_2}]_{\lambda=0}, \tag{41}$$

where $F_S(0) = F_{I_1} + F_{I_2}$ is the free energy of the non-interacting subsystems, and the classical ensemble average

$$[\mathcal{H}_{I_1,I_2}]_{\lambda=0} = \frac{1}{\Omega^{N_{I_1}+N_{I_2}} N_{I_1}! N_{I_2}! Z_{I_1} Z_{I_2}} \int_{I_1} \prod_{i=1}^{N_1} d^3\mathbf{r}_i d\Omega_i \int_{I_2} \prod_{j=1}^{N_2} d^3\mathbf{r}_j d\Omega_j \mathcal{H}_{I_1,I_2} e^{-(\mathcal{H}_{I_1}+\mathcal{H}_{I_2})/k_B\mathrm{T}}. \tag{42}$$

Consider a θ operator [5] which acts on any given system and has the following properties. It leaves the center of mass positions $\mathbf{r}_i$ of particles unchanged, it maps the particle orientations Ω_i on to themselves in such a way that it leaves the integration measure $\prod_i d\Omega_i$ unchanged, and it leaves the Hamiltonian $\mathcal{H}$ invariant. In addition, it reverses the magnetization of every particle. For superparamagnetic particles, spontaneous magnetization reversal acts as a θ operator. For non-superparamagnetic particles, a 180° rotation of particles about an axis of two-fold symmetry suffices as θ operator.

Applying the θ operator to I_1 but not I_2 leaves both $\mathcal{H}_{I_1}$ and $\mathcal{H}_{I_2}$ invariant but reverses the sign of $\mathcal{H}^M_{I_1,I_2}$ while leaving the integration measure unchanged. Hence the average in (42) vanishes and from (41) we get

$$F_S \le F_{I_1} + F_{I_2}. \tag{43}$$

The free energy, therefore, satisfies subadditivity (7).

C. Lower bound on the free energy

The lower bound (8) easily follows if the potential is stable [1,2]. For stable potentials

$$\mathcal{H}_S \ge -\omega V_S, \tag{44}$$

where ω is some positive constant independent of the number of particles. Substituting the lower bound (44) on $\mathcal{H}_S$ in (2) gives an upper bound on the partition function and thus a lower bound (8) on the free energy. Therefore, in this section we will prove the stability for our model.

Let $\mathbf{M}_S(\mathbf{r})$ be the magnetization distribution in a box S, so that $\mathbf{M}_S(\mathbf{r}) = \mathbf{M}_i$ if $\mathbf{r}$ is inside particle i and zero if $\mathbf{r}$ is outside any particle. Let $\mathbf{H}_S^D(\mathbf{r})$ be the magnetic field due to the particles in S. To prove stability we make use of the positivity of field energy. Adding the magnetic self energy of each particle to $\mathcal{H}_S^M$ gives the total energy of the whole system, considered as one magnetization distribution (see Ref. [23] for identities on magnetization distributions),

$$\mathcal{H}_S^T = \mathcal{H}_S^M + \sum_{i=1}^{N_S} E_i^{self} = -\frac{1}{2}\int d^3\mathbf{r}\ \mathbf{H}_S^D(\mathbf{r}) \cdot \mathbf{M}_S(\mathbf{r}). \tag{45}$$

Here $\mathbf{H}_S^D(\mathbf{r})$ is the field, due to all particles inside the container S and

$$E_i^{self} = -\frac{1}{2}\mathbf{M}_i \cdot \int_{v_i} d^3\mathbf{r}\ \mathbf{H}_i^D(\mathbf{r}), \tag{46}$$

where $\mathbf{H}_i^D(\mathbf{r})$ is the field from magnetization $\mathbf{M}_i$ of particle i with volume v_i.

We place a lower bound on $\mathcal{H}$ by a method similar to that of Griffiths [4]. For any magnetization distribution $\mathbf{M}(\mathbf{r})$ and the field $\mathbf{H}^D(\mathbf{r})$ caused by it

$$-\frac{1}{2}\int d^3\mathbf{r}\ \mathbf{H}^D(\mathbf{r}) \cdot \mathbf{M}(\mathbf{r}) = \frac{1}{8\pi}\int d^3\mathbf{r}\ |\mathbf{H}^D(\mathbf{r})|^2 \ge 0. \tag{47}$$

Hence

$$\mathcal{H}_S^M + \sum_{i=1}^{N_S} E_i^{self} \geq 0. \tag{48}$$

Brown [23] rewrites the self energy in (46) as

$$E_i^{self} = 2\pi \sum_{k,l} D_i^{kl} M_i^k M_i^l \quad v_i, \tag{49}$$

where $\mathbf{D}_i$ is the demagnetizing tensor of an "equivalent ellipsoid"; it exists for a particle of any shape [23], and k and l index the components of $\mathbf{D}_i$ and $\mathbf{M}$. Since $\mathbf{D}_i$ is positive definite, with trace equal to 1,

$$E_i^{self} \leq 2\pi M^2 v_i, \tag{50}$$

so that

$$\mathcal{H}_S^M \geq -2\pi M^2 \sum_{i=1}^{N_S} v_i. \tag{51}$$

If the particles are unable to fit inside S without overlap then $\mathcal{H}_S = +\infty$ because of the hard core repulsion. Otherwise, if particles fit inside S without overlap, then $\sum_{i=1}^{N_S} v_i \leq V$ and

$$\mathcal{H}_S = \mathcal{H}_S^M \geq -2\pi M^2 V_S. \tag{52}$$

The free energy of a box $I \in \mathcal{I}$ therefore satisfies the lower bound (8), and we have previously shown that it satisfies the translation invariance (6) and subadditivity (7). The rest of the proof is identical to that of hard core particles polydisperse in size and shape and is omitted.

IV. CONCLUSION

We study the thermodynamic limit of hard core fluids consisting of particles chosen from a distribution that is polydisperse in size and shape. We show that a thermodynamic limit exists with probability 1 and is independent of the choice of particles. The existence of a thermodynamic limit implies shape *independence* of thermodynamic properties. In this section we discuss some models that are not covered by our proof, although we believe they do possess thermodynamic limits.

This paper addressed fluids of particles with hard core interactions and magnetic interactions. We believe the proof could be extended to incorporate interactions that fall off faster than $1/r^3$. One example is a Lennard-Jones fluid with interaction

$$U_{ij} = \frac{A_{ij}}{r^m} - \frac{B_{ij}}{r^n} \tag{53}$$

between particles i and j, where $m > n > 3$ and $A_{ij}, B_{ij} > 0$ are some constants chosen randomly for every pair of particles from some distribution. A “random” Stockmayer fluid is another example, where in addition to the Lennard-Jones interaction described above, each particle i has a randomly chosen magnetic dipole moment μ_i. Another example is a polydisperse charged colloid in ionic solution [29,30] with an interaction such as

$$U_{ij} = \frac{q_i q_j e^{-\kappa r}}{\varepsilon r} \tag{54}$$

where $\kappa > 0$ is the Debye screening length.

For such systems the free energies for a container S composed of two adjacent nonoverlapping rectangular boxes $I_1, I_2 \in \mathcal{I}$ separated by a distance $R \geq R_0 > 0$ satisfy

$$F_S \leq F_{I_1} + F_{I_2} + \Delta_{12}. \tag{55}$$

Here

$$\Delta_{12} = \frac{N_{I_1} N_{I_2} \delta_{12}}{R^{3+\epsilon}} \tag{56}$$

with some $\epsilon > 0$ and δ_{12} depending upon the probability distributions of the pair potentials. Our proof of thermodynamic limit uses a subadditive ergodic theorem which requires strict subadditivity (7) with $\Delta_{12} = 0$. However, we suppose that provided that the probability distributions are sufficiently restricted, a subadditive ergodic theorem similar to that of

Akcoglu and Krengel [10] but with the weaker subadditivity condition (55) will hold and a proof of a thermodynamic limit will follow.

Granular magnetic solids provide other examples of systems outside the realm of our present considerations. Consider a solid system with particles frozen in space but magnetic moments able to rotate with respect to the body of the particles [27] (or a solid containing rotationally free magnetic particles inside cavities [28]) One way to prepare such systems is to freeze the carrier fluid in a colloidal suspension of magnetic hard core particles so that the positions of particles are representative of an equilibrium configuration of the fluid. Our proof does not directly apply to such systems because the infinite system cannot be constructed from finite cubes of frozen particles. A system constructed from finite cubes will have no particles overlapping the boundaries of these cubes and thus the spatial arrangement of particles differs from an equilibrium configuration of the fluid. If the particles are "unfrozen" and frozen back again after their positions have relaxed, then subadditivity (7) no longer holds strictly, though it will hold on average.

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APPENDIX A: EXAMPLES OF ALLOWED PARTICLE DISTRIBUTIONS

Here we present some examples of particle size and shape distributions which obey the packing condition. Our discussion hinges on the ability to pack a monodisperse collection of hard spheres with a hexagonal close packing fraction of $\phi^{hcp} = \frac{\pi}{3\sqrt{2}}$. Our presentation is informal and primarily intended to motivate the form of our packing condition, rather than to achieve rigorous proofs.

Binary mixture of hard core spheres: Consider spherical hard cores of two types with radii r_α and r_β occurring with probabilities p_α and p_β, respectively. A given choice

$\mathbf{c}_N \in \mathcal{C}_N$ of N particles yields N_α spheres of type α and $N_\beta = N - N_\alpha$ of type β. Define the partition function in a volume V as

$$Z_V(\mathbf{c}_N) \equiv \frac{1}{N_\alpha! N_\beta!} \int_V \prod_i dr_i e^{-\mathcal{H}_V(\mathbf{c}_N)/k_B T}. \tag{A1}$$

The factor of $N_\alpha! N_\beta!$ is chosen instead of $N!$ because it yields the usual entropy of mixing [24]. Given a choice $\mathbf{c}_N$, a volume $V(\mathbf{c}_N)$ exists that is sufficiently large that the partition function exceeds a threshold

$$Z_V(\mathbf{c}_N) \geq z_0^N. \tag{A2}$$

We construct the volume $V(\mathbf{c}_N)$ satisfying the inequality (A2) by assigning particles to spherical shells of radius $r'_\alpha = r_\alpha + r_0$ and $r'_\beta = r_\beta + r_0$ where $\frac{4\pi}{3} r_0^3 = z_0$. Shells of type α and β surround volumes $v'_\alpha = \frac{4\pi}{3} r'^3_\alpha$ and $v'_\beta = \frac{4\pi}{3} r'^3_\beta$. If we choose the volume

$$V(\mathbf{c}_N) = (N_\alpha v'_\alpha + N_\beta v'_\beta)/\phi^{hcp} \tag{A3}$$

then the inequality (A2) holds.

To verify this claim, divide the volume into subregions of volumes $N_\alpha v'_\alpha/\phi^{hcp}$ and $N_\beta v'_\beta/\phi^{hcp}$ respectively. Closely pack the α- and β-type shells into their respective subregions and evaluate the configurational integral in Eq. (A1) in two stages. First, confine each particle within its shell and integrate, yielding a contribution of z_0^N. Second, permute identical particles within identical shells, yielding a factor of $N_\alpha! N_\beta!$. Since the combinatorial factor cancels against the normalization of the partition function in Eq. (A1), the partition function $Z_V(\mathbf{c}_N)$ is at least as large as z_0^N.

Now we show that, with probability 1, $V(\mathbf{c}_N)$ does not greatly exceed $N\bar{v}'(z_0)/\phi^{hcp}$, where we identify the mean volume per shell $\bar{v}'(z_0) \equiv p_\alpha v'_\alpha + p_\beta v'_\beta$. Note that $\bar{v}'(z_0)$ approaches the mean particle volume $\bar{v}$ as $z_0 \to 0$. Take a cube Γ of volume

$$V_\Gamma = \frac{N\bar{v}'(z_0)}{\phi^{hcp}}(1+\epsilon) \tag{A4}$$

where ϵ is an arbitrarily small positive number. Divide the set $\mathcal{C}_N$ of choices $\mathbf{c}_N$ into a "packing subset"

$$P_\Gamma = \{\mathbf{c}_N \in \mathcal{C}_N \mid V(\mathbf{c}_N) \leq V_\Gamma\} \tag{A5}$$

and a complementary "nonpacking subset"

$$Q_\Gamma = \{\mathbf{c}_N \in \mathcal{C}_N \mid V(\mathbf{c}_N) > V_\Gamma\}. \tag{A6}$$

Since P_Γ and Q_Γ are complementary subsets, their measures obey $\mu_N(P_\Gamma) + \mu_N(Q_\Gamma) = 1$. By Chebyshev's inequality [18] on the sum of independent random variables we bound the measure of the nonpacking subset by

$$\mu_N(Q_\Gamma) \leq \frac{p_\alpha^2 v_\alpha'^2 + p_\beta^2 v_\beta'^2}{N\bar{v}'(z_0)^2\epsilon^2}. \tag{A7}$$

For sufficiently large N the probability that a choice does not pack into V_Γ vanishes. Thus $V(\mathbf{c}_N) \leq V_\Gamma$ with probability 1 at density

$$\rho \equiv N/V_\Gamma = \frac{\phi^{hcp}}{\bar{v}'(z_0)(1+\epsilon)}. \tag{A8}$$

Therefore, binary mixture of hard spheres obeys the packing condition (5) with $\rho^*(z_0) = \phi^{hcp}/\bar{v}'(z_0)$. Note that $\rho^*(z_0)\bar{v}$ approaches ϕ^{hcp} as $z_0 \to 0$.

Finitely many types of hard spheres: Consider some finite number, t, of types of hard spheres, each type with a different finite radius and a certain probability of occurrence. The argument presented above for a mixture of two types of spheres generalizes easily to the case of $t > 2$. The combinatorial factor in the partition function (A1) generalizes to $\Pi_\alpha N_\alpha!$ and the mean volume per shell generalizes to $\bar{v}'(z_0) \equiv \sum_\alpha p_\alpha v_\alpha'$. An argument similar to that for a binary mixture of hard spheres shows that this distribution satisfies the packing condition (5) with a critical packing density $\rho^*(z_0) = \phi^{hcp}/\bar{v}'(z_0)$. A packing fraction of ϕ^{hcp} is achievable in the limit $z_0 \to 0$, but for finitely many types of hard spheres a higher packing fraction should be achievable because smaller particles can occupy the interstitial sites of larger particles [25].

The distributions above satisfy the packing condition using the prefactor $\Pi_\alpha N_\alpha!$ to define the partition function. However, the prefactor of $(\sum_\alpha N_\alpha)! = N!$ may also be used to define the partition function as in Eq. (2). The logarithm of the ratio of the two prefactors is the entropy of mixing between the particles of various types. As long as the particles are chosen randomly from the distribution and not "unmixed", the factor of $N!$ suffices to give an extensive entropy [6,24]. To show that the distribution satisfies the packing condition using prefactor $N!$, enclose particles in shells so that they have free volume of at least z_0' inside the shell. The partition function is bounded from below by

$$Z_V \geq \frac{\Pi_\alpha N_\alpha!}{N!} {z_0'}^N \geq \left(\frac{z_0'}{t}\right)^N. \tag{A9}$$

Set $z_0' = tz_0$ to show that the distribution satisfies the packing condition (5) as long as t is finite. Now the critical packing density is $\rho^*(z_0) = \phi^{hcp}/\bar{v'}(tz_0)$. As before, $\rho^*(z_0)\bar{v}$ approaches ϕ^{hcp} as $z_0 \to 0$.

Continuous distribution of hard spheres with an upper size cut-off: Consider a continuous distribution of hard spheres with volumes $0 \leq v < v_{max}$. This distribution has essentially an infinite number of types of particles and so our discussion above does not directly apply to it, however, it still satisfies the packing condition (5). To show this, define the partition function with prefactor $N!$ to make the free energy extensive. Break the distribution into a finite number, t, of bins with boundaries $0 < v_1 < v_2 ... < v_t = v_{max}$. Let the i^{th} bin $\mathcal{B}_i$ contain all the particles with $v_{i-1} \leq v < v_i$. Enclose every particle in bin $\mathcal{B}_i$ within a shell of volume

$$v'_{\mathcal{B}_i} = \frac{4\pi}{3}\left\{\left(\frac{3v_i}{4\pi}\right)^{1/3} + \left(\frac{3z_0}{4\pi}\right)^{1/3}\right\}^3 \tag{A10}$$

so that the largest particle in $\mathcal{B}_i$ has a free volume of at least $z_0' = tz_0$, then apply the same argument as for finitely many types of spheres. The resulting $\rho^*(z_0) = \phi^{hcp}/\bar{v'}(tz_0)$ results in a suboptimal achievable packing fraction $\phi = \rho^*(z_0)\bar{v} = \phi^{hcp}\bar{v}/\bar{v'}(tz_0) < \phi^{hcp}$ due to the bin width and the choice of prefactor $N!$. By using a sufficiently large but finite number of bins and taking $z_0 \to 0$, a packing fraction arbitrarily close to ϕ^{hcp} can be achieved. As in the case of discrete distributions, for a continuous distribution of hard spheres one expects a higher packing fraction than that of a monodisperse system should be achievable [25].

Continuous distribution of hard spheres with no particle size cut-off: Now we consider a continuous distribution of hard core spheres such that the particle size has no upper limit. To ensure that the large sized particles occur sufficiently infrequently, we assume that there exists a particle volume v^* such that the probability of a particle with volume greater than v_0 for any $v_0 > v^*$ falls off as

$$\mu_1(v > v_0) \leq \frac{\gamma}{v_0^{1+\delta}}, \tag{A11}$$

where γ and δ are positive constants. Note that this condition guarantees the existence of a mean particle volume but not the existence of higher moments.

To show that this distribution satisfies the packing condition (5) we break the distribution into a finite number, $t+1$, of bins with boundaries $0 < v_1 < v_2 ... < v_{t-1} < v_t < \infty$. We presume that $v_{t-1} > v^*$. The next-to-last bin $\mathcal{B}_t$ includes all the particles with $v_{t-1} \leq v < v_t$ and the last bin $\mathcal{B}_{t+1}$ contains all the particles with $v_t \leq v < \infty$. We now send v_t to infinity in such a manner that $\mathcal{B}_{t+1}$ is empty with high probability but the maximum particle size in $\mathcal{B}_t$ grows in a controlled fashion. To show that the distribution satisfies the packing condition (5) we first show that the set of choices with no particle in $\mathcal{B}_{t+1}$ is a set of measure 1. Then we show that in this set there is a subset of measure 1 of choices which have a partition function of at least z_0^N.

The probability that a collection of N particles randomly chosen from the distribution contains at least one particle in the last bin $\mathcal{B}_{t+1}$ is bounded by

$$\mu_N(\mathbf{c}_N \mid \text{at least one particle in } \mathcal{B}_{t+1}) \leq \frac{N\gamma}{v_t^{1+\delta}}. \tag{A12}$$

We wish to avoid all choices with at least one particle in $\mathcal{B}_{t+1}$. To ensure that the probability of such choices goes to zero for large N, v_t must grow faster than $N^{1/(1+\delta)}$. At the same time v_t must grow slower than N to ensure that the largest particles in $\mathcal{B}_t$ are much smaller than the system size. Hence let v_t grow proportional to $N^{1/(1+\frac{\delta}{2})}$, so that

$$\mu_N(\mathbf{c}_N \mid \text{at least one particle in } \mathcal{B}_{t+1}) \leq \frac{\gamma'}{N^{\frac{\delta}{2+\delta}}} \to 0, \tag{A13}$$

where γ' is some constant. For large N, the probability approaches 1 that no particle is in bin $\mathcal{B}_{t+1}$.

Now consider the particles in bin $\mathcal{B}_t$. The next-to-last bin $\mathcal{B}_t$ must be treated specially because the largest particle size in $\mathcal{B}_t$ diverges as the system size to goes infinity. Enclose each particle j (with volume v_j) in $\mathcal{B}_t$ inside its own shell with volume v'_j so that it has a free volume of $z'_0 = tz_0$. Using condition (A11) the total volume of the shells corresponding to bin $\mathcal{B}_t$ (averaged over choices $\mathbf{c}_N$) obeys

$$\Big\langle \sum_{v_j \in \mathcal{B}_t} v'_j \Big\rangle \leq \frac{\gamma(1+\delta)}{\delta} \frac{N}{v_{t-1}^{\delta}}. \tag{A14}$$

Since the volume of the system is proportional to N, the volume fraction occupied by shells corresponding to bin $\mathcal{B}_t$ is proportional to $v_{t-1}^{-\delta}$. This volume fraction can be made arbitrarily small by choosing a sufficiently large v_{t-1}. We assume that the N_t particles in bin $\mathcal{B}_t$ (enclosed in their shells) can be packed inside a small region of the system in $N_t!$ different ways with high probability (tending to 1 as N goes to infinity).

The particles in the remaining bins $\mathcal{B}_1, ..., \mathcal{B}_{t-1}$ have a partition function of at least $z_0^{N-N_t}$ in the remaining volume of the system with high probability (tending to 1) as we showed previously for a continuous distribution of spheres with an upper size cut-off. Therefore, these particles together with the particles in $\mathcal{B}_t$ satisfy the packing condition (5).

Non-spherical particles: Finally, consider a distribution of non-spherical particles. To show that the distribution satisfies the packing condition (5), enclose each particle inside a spherical shell with a diameter equal to the largest dimension of the particle. If the volume of the shells satisfy condition (A11) then the rest of the argument is the same as that of a continuous distribution of hard spheres. Although this argument shows the existence of a finite particle number density $\rho^*(z_0)$, it does not guarantee the existence of a finite packing fraction. In fact, it is possible to have distributions with oddly shaped particles (fractals for example) so that a finite $\rho^*(z_0)$ exists but the particle packing fraction is zero.

APPENDIX B: VARIANCE OF FREE ENERGY DENSITY FOR CUBES

To show the variance relation (11) consider two adjacent nonoverlapping cubes Γ_k^l and Γ_k^m such that $I_k = \Gamma_k^l \cup \Gamma_k^m$ is a rectangular box. Using the subadditive relation (7) we get

$$f_{I_k} \leq \frac{1}{2}(f_{\Gamma_k^l} + f_{\Gamma_k^m}). \tag{B1}$$

Adding ω_A (see lower bound (8)) to both sides of (B1) and squaring gives

$$f_{I_k}^2 + 2\omega_A f_{I_k} + \omega_A^2 \leq \frac{1}{4}(f_{\Gamma_k^l} + f_{\Gamma_k^m})^2 + \omega_A^2 + \omega_A(f_{\Gamma_k^l} + f_{\Gamma_k^m}). \tag{B2}$$

Averaging both sides over all choices of particles we write

$$\langle f_{I_k}^2 \rangle + 2\omega_A \langle f_{I_k} \rangle + \omega_A^2 \leq \frac{1}{2}\langle f_{\Gamma_k}^2 \rangle + \frac{1}{2}\langle f_{\Gamma_k} \rangle^2 + 2\omega_A \langle f_{\Gamma_k} \rangle + \omega_A^2. \tag{B3}$$

Subtracting $\omega_A^2 + \langle f_{I_k}^2 \rangle + 2\omega_A \langle f_{I_k} \rangle$ and rearranging terms on the right-hand side gives

$$\langle (f_{I_k} - \langle f_{I_k} \rangle)^2 \rangle \leq \frac{1}{2}\langle (f_{\Gamma_k} - \langle f_{\Gamma_k} \rangle)^2 \rangle + \langle f_{\Gamma_k} \rangle^2 - \langle f_{I_k} \rangle^2 + 2\omega_A(\langle f_{\Gamma_k} \rangle - \langle f_{I_k} \rangle). \tag{B4}$$

Using the bound

$$\langle f_{\Gamma_k} \rangle + \langle f_{I_k} \rangle \leq -2k_B \mathrm{T} \ln z_0 \equiv 2\omega_B, \tag{B5}$$

we get

$$\langle (f_{I_k} - \langle f_{I_k} \rangle)^2 \rangle \leq \frac{1}{2}\langle (f_{\Gamma_k} - \langle f_{\Gamma_k} \rangle)^2 \rangle + 2(\omega_A + \omega_B)(\langle f_{\Gamma_k} \rangle - \langle f_{I_k} \rangle). \tag{B6}$$

Both $\langle f_{I_k} \rangle$ and $\langle f_{\Gamma_k} \rangle$ go to the same limit f_Γ since $\langle f_{\Gamma_{k+1}} \rangle \leq \langle f_{I_k} \rangle \leq \langle f_{\Gamma_k} \rangle$. Therefore, we can bound the second term on the right in (B6) below any $\epsilon' > 0$ for sufficiently large k. It follows that

$$\langle (f_{I_k} - \langle f_{I_k} \rangle)^2 \rangle \leq \frac{1}{2}\langle (f_{\Gamma_k} - \langle f_{\Gamma_k} \rangle)^2 \rangle + \epsilon'. \tag{B7}$$

By stacking two rectangular boxes I_k together to form a square slab, then putting together two adjacent slabs, we construct a cube Γ_{k+1}. The variance of the cube Γ_{k+1} is related to that of Γ_k by

$$\langle (f_{\Gamma_{k+1}} - \langle f_{\Gamma_{k+1}} \rangle)^2 \rangle \leq \frac{1}{8}\langle (f_{\Gamma_k} - \langle f_{\Gamma_k} \rangle)^2 \rangle + \epsilon, \tag{B8}$$

where $\epsilon = (1 + \frac{1}{2} + \frac{1}{4})\epsilon' = \frac{7}{4}\epsilon'$.

APPENDIX C: CONVEXITY AND CONTINUITY OF THE FREE ENERGY DENSITY FOR CUBES

Consider a cube Γ_k with volume V_{Γ_k} that contains N_k particles. Since N_k is an integer, the free energy density $f_{\Gamma_k}(\rho, \mathbf{c}_{N_k})$ is defined only for discrete values of ρ. Since $f_{\Gamma_k}(\rho, \mathbf{c}_{N_k})$ is a random variable, a linear interpolation to include fractional number of particles is not possible. However, the average free energy density $\langle f_{\Gamma_k}(\rho)\rangle$ is not random and we define $\langle f(\rho)\rangle$ for all values of ρ by linear interpolation between values of ρ that correspond to integer values of N_k.

Now consider a cube Γ_{k+1} consisting of 4 cubes Γ_k each containing N_k' particles and 4 cubes Γ_k each containing N_k'' particles. From subadditivity (7) of free energy, and averaging over all possible choices of particles in the cubes Γ_k, it follows that

$$\Big\langle f_{\Gamma_{k+1}}(\rho)\Big\rangle \leq \frac{1}{2}\Big(\Big\langle f_{\Gamma_k}(\rho')\Big\rangle + \Big\langle f_{\Gamma_k}(\rho'')\Big\rangle\Big), \tag{C1}$$

where $\rho' = N_k'/V_{\Gamma_k}$, $\rho'' = N_k''/V_{\Gamma_k}$ and $\rho = (\rho' + \rho'')/2$. By linear interpolation Eq. (C1) holds for any ρ' and ρ''. Taking the limit $k \to \infty$ gives

$$\Big\langle f_{\Gamma}(\rho)\Big\rangle \leq \frac{1}{2}\Big(\Big\langle f_{\Gamma}(\rho')\Big\rangle + \Big\langle f_{\Gamma}(\rho'')\Big\rangle\Big). \tag{C2}$$

Therefore, $\langle f_\Gamma(\rho)\rangle \equiv \bar{f}_\Gamma(\rho)$ is a convex function of ρ. Since $\bar{f}_\Gamma(\rho)$ is a bounded function of ρ, it is also continuous function of ρ [26].

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FIGURES

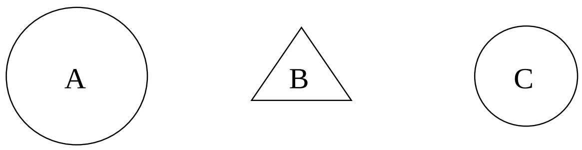

FIG. 1. An example of a size and distribution of particles. The hard core particles A, B, C are chosen with fixed probabilities.

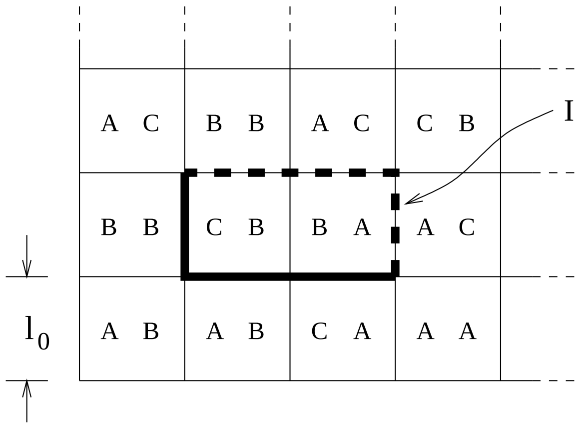

FIG. 2. One particular choice of particles from the distribution in Fig 1. into basic cubes, with $N_0 = 2$ particles in each basic cube. The box $I = [(l_0, l_0), (3l_0, 2l_0))$ in this example is assigned particles C, B, B, and A. For easy visualization we show the figure in two-dimensions instead of the actual case of three dimensions.

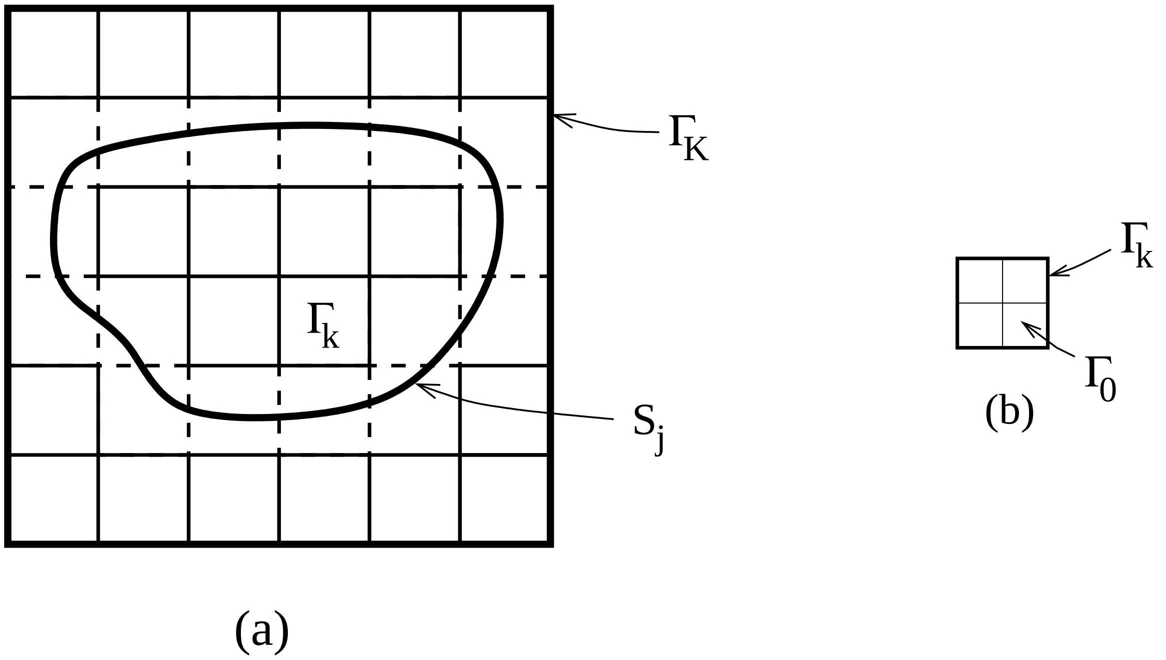

FIG. 3. (a) A cross-section of an arbitrary shape S_j. The space inside S_j, and the space between S_j and Γ_K, is maximally filled by cubes Γ_k. Dashed lines indicate the cubes that intersect the boundary of S_j. The volume of cubes Γ_k that intersect S_j becomes negligible in comparison to the volume of S_j as the size of S_j goes to infinity and the size of Γ_k grows less rapidly than S_j. (b) A cube Γ_k in d dimensions consists of 2^{kd} basic cubes Γ_0. In this case $k = 1$ and $d = 2$.

FIG. 4. (a) Particle shapes with a two-fold symmetry perpendicular to their magnetization. The arrow indicates the direction of magnetization. (b) Particle shapes lacking two-fold symmetry perpendicular to their magnetization.