Cluster crystals with combined soft and hard-core repulsive interactions

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(Dated: November 1, 2018)

Particle systems interacting with a soft repulsion, at thermal equilibrium and under some circumstances, are known to form cluster crystals, i.e. periodic arrangements of particle aggregates. We study here how these states are modified by the presence of an additional hard-core repulsion, accounting for particle size. To this end we consider a two-dimensional system of Brownian particles interacting through a potential which includes a hard-core and a soft-core (of the GEM-α type) repulsive terms. The system shows different phases, and we focus in the regime where cluster crystals form. We consider two situations: the low-temperature one in which particles inside the clusters also show an ordered structure (crystal cluster-crystal phase), and the one occurring at higher temperature in which particles within the clusters are spatially disordered (fluid cluster crystal). An explicit expression for the energy in terms of the typical distance between clusters and the typical distance of the particles within the clusters is obtained for vanishing temperature, from which mean mean inter- and intra-cluster distances are obtained. Finite-temperature corrections are also discussed considering explicitly the role of the entropy.

PACS numbers:

I. INTRODUCTION

Particles interacting via soft-core repelling forces may crystallize in equilibrium into ordered structures, with a unit cell composed of a closely packed cluster of particles [1–7]. This is a particularly relevant situation for some polymers, dendrimers or colloidal solutions, where the effective potentials between their centers of mass are soft and repulsive [4, 8, 9]. This phase, called cluster crystal, occurs for low temperatures and large enough density and packing fraction.

This type of systems has been studied by using a variety of methods, from Monte Carlo to density functional theory [4, 5], or in the related Dean-Kawasaki equation approach [10]. A mathematical criterion needed for the formation of cluster crystals is that the Fourier transform of the interparticle potential, \( \bar{V}(k) \), should take negative values for some values of \( k \) [4, 5, 10]. For the commonly studied generalized exponential model (GEM-α), \( V(r) = \epsilon \exp(-r/R)^\alpha \) - which is an example of soft potential [8] - with \( \epsilon \) an energy scale and \( R \) the typical interaction range, this happens when \( \alpha > 2 \). The occurrence of cluster crystals in GEM-α potentials with \( \alpha > 2 \) is related to the fact that as \( \alpha \) increases the potential becomes more box-like shaped. The physical mechanism leading to the cluster crystals is the balance between the repulsive forces among particles inside a cluster, and the forces from neighboring ones [10].

The natural extension of considering a hard-core contribution into the potential, taking into account the finite size and impenetrable character of a core part of the interacting particles, was considered in [11]. A problem to study this type of system within a continuous-density description is that this approach leads to the consideration of the Fourier transform of the potential, which in general is not well-defined in the hard-core case. The authors of [11] use instead a lattice model where the lattice constant equals the particle size and the hard-core repulsion is implemented by imposing single occupancy per site. Thus they generalize the soft-potential criterion for the appearance of cluster crystals to include terms depending on the occupied volume fraction. However, this lattice model cannot distinguish ordered from disordered states within the clusters. To avoid this [11] also introduced an off-lattice model with the particular type of potentials known as hard-core/soft-shoulder potentials. Further studies with the same potentials are found in [12, 13] where, in particular, finite temperature corrections and detailed phase diagrams are presented.

In this work, we focus on the study of two-dimensional off-lattice systems with repulsive interaction potentials related to the well-studied hard-core/soft-shoulder case but more general than it. Specifically, we consider a soft repulsion of the GEM-α type at large distances, complemented by a strongly repulsive core behaving as \( r^{-b} \) at short distances. We keep the name of ‘hard-core’ for this part of the potential, although it is not strictly impenetrable. Under suitable parameters, in particular at low temperature, cluster-crystal phases are found. Our main question is to understand how the hard-core power-law potential changes the equilibrium configurations of particles interacting through the GEM-α potential. To understand the structures found we compute the energy of the system by considering both the interactions between clusters and the interactions among particles within clusters. For this last contribution, at variance with previous studies [11–13], we explicitly take into account the intraaggregate structure, i.e., whether the particles may order periodically or not inside every cluster. Mean inter- and intra-cluster distances are then obtained from en-
ergy minimization. We validate our results with numerical simulations of an ensemble of interacting Brownian particles in a thermal bath. Temperature corrections are also considered to estimate the typical cluster size, which is different at very low temperature, when the within-cluster distribution of the particles shows an ordered structure, with respect to higher temperatures, when the clusters are in a fluid/gas state.

The paper is organized as follows. In Section II we introduce the model, discuss the role of the spatial scales in the potential, and present the system’s phases that will be studied. In Section III we derive an analytical expression for the energy of the system in the crystal cluster phase, in the limit of small temperatures. In the subsequent section IV we compute some temperature effects on cluster characteristics. We conclude with a summary and discussion in Sec. V.

II. MODEL AND CLUSTER CRYSTAL PHASES

As one of the ways to obtain thermal equilibrium configurations under the type of interactions described above, we consider a $d$-dimensional system of $N$ interacting Brownian particles of unit masses in contact with a thermal bath. We restrict to a regime of very large friction which allows us to neglect the inertial terms and to assume directly an overdamped dynamics:

$$\dot{x}_i = -\nabla_i V(x_1,...,x_N) + \sqrt{2D} \eta_i, \quad i = 1,...,N,$$

(1)

where the noise vector, $\eta$, with component $\eta_i$, verifies $\langle \eta_i \rangle = 0$ and $\langle \eta_i(t)\eta_m(t') \rangle = \delta(t-t')\delta_{i,m}$, with $l,m = 1,...,d$. The diffusion coefficient $D$ is proportional to the temperature through the Einstein relation $D = k_B T$ when time is measured in units of the inverse friction coefficient. The potential, $V$, is pairwise and contains two parts, a hard-core repulsive part $V_h$ (they act at different scales as detailed later on):

$$V(x_1,...,x_N) = \sum_{1 \leq i < j \leq N} [V_h(|x_i - x_j|) + V_s(|x_i - x_j|)].$$

(2)

We restrict to $d = 2$ and study all along this paper the particular cases of $V_h(r) = \epsilon h (\frac{r}{\rho_0})^b$ and $V_s(r) = \epsilon_s \exp[-(r/R)^\alpha]$, with $r = |x|$. $V_h$ is the GEM-$\alpha$ potential which accounts for an effective soft repulsive interaction with a typical length scale $R$ and energy scale $\epsilon_s$. $V_h$, modeling a hard-core, is a standard power-law repulsion where $\rho_0$ stands for the typical length scale for the size of the particles. $\epsilon_h$ is an energy scale which can be absorbed in the definition of $\rho_0$, since it always appears in the combination $\epsilon h \rho_0^b$. However, we keep this parameter explicit throughout the paper, as it helps to identify the terms in our expressions coming form the hard core. In the numerics it will be fixed as $\epsilon_h = \epsilon_s$. Despite the particular choice of the potentials we point out the generality of the arguments presented below.

In the absence of the hard-core potential the behavior of the system is well-understood: for $\alpha > 2$, small enough temperature, large enough numerical density, $\rho_0 = N/L^d$, and large packing fraction, $\phi = \rho_0 R^d$, cluster crystals are formed in which (point) particles aggregate in clusters separated by a distance proportional to $R$, with particles randomly moving inside each cluster [10]. Unveiling the effects of the hard-core potential on this phase is the main purpose in what follows. Note the difference with other studies considering cluster phases with short-range attraction and long-range repulsion [14–16]. In our setting, there is no attraction at any scale.

The shape of the total potential $V = V_h + V_s$ is shown in Fig. 1 for the special case $\alpha = 3$ and $b = 6$. If there is no scale separation, $\rho_0 \sim R$ (green-dashed and blue-dotted lines in Fig. 1), the potential behaves effectively as just a hard-core repulsive one, since all of the features of the soft-core part are masked. This is qualitatively similar to setting $V_s = 0$. In this case, particles freeze at low temperatures forming a hexagonal lattice. We will not discuss here the subtleties associated with the nature of this type of two-dimensional crystallization, see for example [17]. The interesting regime, assumed in the rest of the paper, occurs when $\rho_0 \ll R$ (red solid line in Fig. 1): the potential has an abrupt decrease up to the scale $\rho_0$, followed by a smoother one, as shown in the figure inset.

FIG. 1: (a) Potential given by $V_s(r) + V_h(x)$ with $V_h(r) = \epsilon h \exp (-(r/R)^\alpha)$ and $V_s(r) = \epsilon_s \exp[-(r/R)^\alpha]$, with $r = |x|$. $V_h$ is the GEM-$\alpha$ potential which accounts for an effective soft repulsive interaction with a typical length scale $R$ and energy scale $\epsilon_s$. $V_h$, modeling a hard-core, is a standard power-law repulsion where $\rho_0$ stands for the typical length scale for the size of the particles. $\epsilon_h$ is an energy scale which can be absorbed in the definition of $\rho_0$, since it always appears in the combination $\epsilon_h \rho_0^b$. However, we keep this parameter explicit throughout the paper, as it helps to identify the terms in our expressions coming form the hard core. In the numerics it will be fixed as $\epsilon_h = \epsilon_s$. Despite the particular choice of the potentials we point out the generality of the arguments presented below.

A. Cluster crystal phases

As shown in Fig. 2, numerical simulations in a two-dimensional square box of size $L$ with periodic boundary conditions show a phenomenology consistent with [11]. In particular, for $\alpha = 3$, $b = 6$ and restricting to densities and packing fractions large enough, cluster crystal
phases are found: at low-enough temperature, particles aggregate in clusters which arrange hexagonally. Moreover, the average population of each cluster, \( N_c \), increases with \( \phi \). The inter-cluster distance, \( \bar{x} \), is relatively insensitive to \( \phi \), increasing just with \( R \). These are the usual properties of cluster crystals [4, 5, 10].

We discuss the effect of the temperature \( T \), or equivalently of the diffusion coefficient \( D = k_B T \), by evaluating the microscopic structure of the system via the radial distribution function \( g(r) = \rho_0^{-1} \langle \sum_{i \neq 0} \delta (\mathbf{x} - \mathbf{x}_i) \rangle \), where a target particle is at the origin, the sum is over the other particles, and the brackets indicate an equilibrium temporal (long-time) or thermal average, and also a circular average over positions \( \mathbf{x} \) with the same modulus \( |\mathbf{x}| = r \).

The comparison of \( g(r) \) at small distances with typical radial distribution functions of a simple solid/liquid/gas allows us to identify solid-, liquid- and gas-like aggregation phases inside the clusters, which coexist with the cluster crystal structure at much larger distances. Since the number of particles in the clusters is small, these states cannot be interpreted as real distinct macroscopic phases. For this reason, a rigorous discussion about phase transitions is meaningless and we restrict our considerations to the qualitative configuration of the system, for which the following observations are made:

1. For small temperatures, particles inside each cluster are almost frozen, showing a hexagonal arrangement. This is the ordered crystal phase identified in [11], which is shown in the top row of Fig. 2. The left panel shows the crystal of clusters, and the right one a zoom of one cluster, with the particles perfectly ordered. The lower row shows \( g(r) \) at the scale of the clusters (left panel) and a zoom into the peak in the region \( r \approx r_0 \), displaying the crystalline ordering of the particles within clusters (right panel). From the position of the peaks in both figures, we can obtain the equilibrium distance among clusters \( \bar{x}_c \approx 1.4R \) (left panel) or among particles \( \bar{x}_c \approx 4.05r_0 \) (right). As in a solid, particles fluctuate around their equilibrium positions, but these fluctuations are very small compared to \( \bar{x}_c \). We observe that in the steady state, after a long time transient, the hexagonal clusters become aligned so that the lines joining their centers coincide with their apothems: the crystal is completely ordered.

2. Increasing the temperature, particle positions disorganize and a liquid-like phase appears inside each cluster. As in a simple liquid, particles move around the whole cluster volume. In Fig. 3, \( g(r) \) at the small scales is shown (green \( D = 10^{-3} \) and yellow \( D = 10^{-3} \) lines), revealing a crossover from solid to fluid characteristics.

3. A further increase of \( T \) produces the growth of the clusters volume. Particles within each cluster form a gas-like phase, as revealed by the absence of well-defined secondary peaks in Fig. 3 (red \( D = 10^{-2} \) line).

4. Further increase of the diffusion coefficient or temperature makes the clusters disappear, leaving a global fluid phase. On the other hand, by increasing \( \phi \), we observe the lamellar and micelle phases described in [11]. However, as mentioned in the introduction, we restrict our study to the range of temperatures or volume fractions where only the different types of cluster crystals appear.

III. CLUSTER ENERGY

We now set-up an energy calculation which is useful to understand the observed structures and phenomenology, in particular, the steady state properties of the system: the distance between clusters, the lattice type and the average size of the clusters. In this Section we restrict to very small \( T \), i.e., to the crystal cluster-crystal phase, numerically discussed in the previous Section. In
FIG. 3: $g(r)/g_m$ ($g_m$ is the maximum value of $g$) at small scales $r \approx r_0 << R$ for different diffusion coefficients $D = k_B T = 10^{-6}, 10^{-4}, 10^{-2}$, respectively, blue rhombus, green upper triangle, orange lower triangle and red pentagon. On the right we show a snapshot of within-cluster particle distributions corresponding to each of the three lower temperatures.

Remaining parameters: $\alpha = 3, b = 6, L = 1, N = 10^3, r_0 = 10^{-3}, R = 10^{-1}, \epsilon_s = \epsilon_h = 1$.

In this regime any entropic contribution does not affect significantly the free energy, as expected in the solid state. In the next Section we will consider finite temperature corrections, and the role of the entropy will be explicitly taken into account. Note that, as mentioned in the introduction, we avoid any description based on the coarse-grained density of particles. This is similar to the off-lattice approach followed by [11] for the hard-core/soft-shoulder case, but extended here to our more general class of potentials.

We rewrite the total energy into two contributions: a self-energy of the clusters themselves, $E_C$, and an interaction energy among them, $E_I$. Two main quantities are fundamental: the mean inter-cluster distance, $\bar{x}$, and the mean inter-particle distance inside a cluster, $\bar{x}_c$. Indeed, the number of clusters in the system, $N_c$, can be estimated as $n_c = \chi L^d/\bar{x}_c^d$, (for arbitrary dimension $d$) where $\chi$ is a parameter which depends on the lattice, for instance $\chi = 1$ for a square lattice and $\chi = 2/\sqrt{3}$ for a triangular one. If we denote as $N_c$ the average number of particles of each cluster, then $N = n_c N_c$, so that we can write $N_c = \bar{x}_c^d \rho_0/\chi$. The average size of the cluster, $\bar{x}_c$, can be estimated from $\bar{x}$ and $N_c$, considering the hexagonal arrangement of the intra-cluster particles.

In the following, we work in 2 dimensions but our approach can be extended to three dimensional systems. As mentioned, for small enough temperature we can neglect entropic contributions and the equilibrium properties are all determined by the total energy $E = E_C + E_I$, where:

$$E_C = n_c \sum_{1 \leq i < k} N_c \left[ V_h(|x_i - x_k|) + V_s(|x_i - x_k|) \right].$$

Since $r_0$ is very small, and $V_s$ decays fast with distance, it is a reasonable approximation for the intercluster energy to consider only interactions of particles in neighboring clusters, so that:

$$E_I \approx n_c \frac{\gamma_f}{2} E_I^{a,b}$$

$$= n_c \frac{\gamma_f}{2} \sum_{k_h,i_h=1}^{N_c} \left[ V_h(|x_{i_h} - x_{k_h}|) + V_h(|x_{i_h} - x_{k_h}|) \right],$$

where $E_I^{a,b}$ is the interaction energy between two neighboring clusters, that we denote by $a$ and $b$, and $x_{i_h}$ ($i_h = 1, ..., N_c$) is the position of the $i$-th particle in the cluster $a$. The constant $\gamma_f$ is the number of first neighbors in the lattice in which the clusters arrange (in two dimensions $\gamma_f = 6$ for a hexagonal lattice, or $\gamma_f = 4$ for a square lattice). Since we assume a separation of scales of both potential terms, we consider $\bar{x}$ and $\bar{x}_c$ independent variables and look for an expression for the energy such that $E = E(\bar{x}, \bar{x}_c) = E_I(\bar{x}, \bar{x}_c) + E_C(\bar{x}, \bar{x}_c)$. As already mentioned, for $T$ small enough, the equilibrium configuration is the one that minimizes the total energy with respect to $\bar{x}$ and $\bar{x}_c$. Let us point out that, because of the relation between $\bar{x}$ and $N_c$, at constant density the minimization with respect to $\bar{x}$ is formally equivalent to the one with respect to $N_c$, exploited within the density functional approach in previous works [18, 19] for purely soft-core potentials.

To proceed we introduce the particular forms of $V_h$ and $V_s$ and make use of their properties. In the following we are labeling different clusters with letters $a, b, ..., c$ and the particles with indices $i, j, ..., n$ or if we want to specify the $i$-th particle of cluster $a$ we use $i_a = 1, ..., N_c$. Let us first work out the self-interaction cluster energy:

$$E_C = n_c \sum_{1 \leq i < k} \left[ \epsilon_s e^{-\gamma_f x_i (x_i - x_k)/R} + \epsilon_h \left( \frac{r_0}{|x_i - x_k|} \right)^b \right]$$

$$= n_c \epsilon_s \left( \frac{N_c}{2} (N_c - 1) + \sum_{i < k} O(x_{ik}/R) \right)$$

$$+ n_c \epsilon_h \sum_{i < k} \left( \frac{r_0}{x_{ik}} \right)^b$$

$$\approx n_c \epsilon_s \frac{N_c}{2} (N_c - 1) + n_c \epsilon_h \gamma_C \left( \frac{r_0}{\bar{x}} \right)^b,$$

where $x_{ik}$ is the distance between the $i$-th and $k$-th particle in one cluster, so that $|x_{ik}| < d_c$, where $d_c$ is the diameter of the cluster, which is also smaller than the inter-cluster distance, $d_c < x$. The last approximation in Eq. (5) is obtained by considering $|x_{ik}|/R < 1$, and also restricting interactions with the hard-core potential to the first neighbors. Now, the constant $\gamma_C$ is the number of first neighbors in the intra-cluster lattice, ($\gamma_C = 6$ in the hexagonal case). $E_C$ in Eq. (5) contains a term coming from the soft-core part of the potential, and another involving the hard-core one, which takes into account the internal structure of the clusters. Using $N = n_c N_c$ and

$$\epsilon_s \epsilon_h \left( \frac{r_0}{|x_i - x_k|} \right)^b$$
\[ N_c = \frac{\bar{x}^2 \rho_0}{\chi}, \] we find (neglecting a constant term):
\[
E_C = N \left( \epsilon_0 \frac{\bar{x}^2}{\chi} + \epsilon_h \gamma C \left( \frac{r_0}{\bar{x}} \right)^b \right). \tag{6}
\]

We can see from this expression that the cluster self-energy favors the equilibrium configuration where clusters are near (because of the term \( \propto \bar{x}^2 \)), but with particles inside them far from each other (because of the term proportional to \( 1/\bar{x}^b \)).

Let us next obtain an expression for the interaction energy among first neighbors clusters, \( E_I \), starting from Eq. (4). The distance between two particles in different clusters can be written as \([x_{a} - x_{b}] = [(\bar{x} + z_{a}k_{a})\hat{z} + y_{a}k_{a}\hat{y}],\) where \( \bar{x} + z_{a}k_{a} \) is the distance between the particles of two different clusters projected onto the direction of the unit vector \( \hat{z} \) parallel to the line connecting cluster centers; \( y_{a}k_{a} \) is the projection of the same distance on the orthogonal axis of unit vector \( \hat{y} \). In this way we have separated the distance between two particles in different clusters as a sum of the distance between the centers of the two clusters, \( \bar{x} \), and the remaining part \( z_{a}k_{a} \), which is smaller than the diameter of the cluster \( d_c \). Taking into account the specific shape of the potentials: 
\[
E_I = n_c \frac{x}{2} \sum_{k_{a}=1}^{N_c} \left[ \epsilon_0 e^{-((\bar{x} + z_{a}k_{a})\hat{z} + y_{a}k_{a}\hat{y})/R} \right]^{b} + \epsilon_h \left( \frac{r_0}{((\bar{x} + z_{a}k_{a})\hat{z} + y_{a}k_{a}\hat{y})} \right)^{b} \approx n_c \frac{x}{2} \sum_{k_{a}=1}^{N_c} \left[ \epsilon_0 e^{-((\bar{x} + z_{a}k_{a})\hat{z} + y_{a}k_{a}\hat{y})/R} \right]^{b}, \tag{7}
\]

where we have neglected the term \( O(r_0/((\bar{x} + z_{a}k_{a})\hat{z} + y_{a}k_{a}\hat{y})) \ll 1 \), since \( \bar{x} \gg r_0 \). The role of the hard-core is present in this expression through \( z_{a}k_{a} \) and \( y_{a}k_{a} \) in the exponential, which is not negligible and gives a non-trivial contribution. Note that taking into account the microscopic structure inside a cluster is crucial for the micro-scale: the appearance of \( z_{a}k_{a} \) and \( y_{a}k_{a} \) in Eq. (7) gives the only dependence on \( z \) that can balance the \( 1/\bar{x}^b \) term appearing in the cluster self-energy Eq. (6). If this dependence on \( \bar{x} \) is neglected, it would be impossible to find any equilibrium value, \( \bar{x} \).

To close our problem we need to write the distance \(|(\bar{x} + z_{a}k_{a})\hat{z} + y_{a}k_{a}\hat{y}|\) in terms of \( \bar{x} \) and \( \bar{z} \), in order to express \( E_I \) in terms of these two distances. One of the possible approximations, which we call line approximation (LA), consists in neglecting the \( y \) coordinate of the particle, so that each hexagonal cluster becomes compressed onto a line. Since, as noted above, the direction \( z \) joining cluster centers coincides with the hexagonal cluster apothems, the LA considers all particles concentrated on these apothems. See Fig. 4, panel d), for a drawing of this procedure. By calling \( n \) the number of particles located on one external side of a hexagonal cluster, the approximation projects particle positions into one of the \( 2n - 1 \) sites, separated by a distance \( \bar{x} \sqrt{3}/2 \), located in a line along the \( z \) direction (see Fig. 4d). Each site, now, contains more than one particle, with a degeneracy which is maximum in the middle of the cluster and minimum at its extremal points. \( n \) is related to \( N_c \) by: \( N_c = 3n/2 \). Since \( N_c = \bar{x}^2 \rho_0 / \chi \), we can express \( n \) as a function of \( \bar{x} \). For large hexagons \( n \gg 1 \), we have \( n \approx \bar{x} (\rho_0/3\chi)^{1/2} \). Using that \( n_c = N/N_c = N/\chi \rho_0 \bar{x}^2 \), we can easily find an approximation for \( E_I \):
\[
E_I \approx \epsilon_n N \frac{\bar{x}}{\chi} \frac{1}{2} \sum_{\mu_{h},\mu_{b}=1}^{2n-1} g^{\mu_{h}} g^{\mu_{b}} e^{-((\bar{x} + (\mu_{h} + \mu_{b} - 2n) \bar{z})/R)}^{b}, \tag{8}
\]

where the sum is over all sites, \( \mu_{h}, \mu_{b} \), in the lines that approximate the particle positions in two contiguous clusters. The product \( g^{\mu_{h}} g^{\mu_{b}} \) gives the degeneracy arising from the number of particles associated to each site in each of the two lines: \( g^{\nu} = n - 1 + \nu \) for \( \nu \in [1, n] \) and \( g^{\nu} = 3n - 1 - \nu \) for \( \nu \in [n + 1, 2n - 1] \) (Fig. 4d).

Unlike the expression for the cluster self-energy, Eq. (6), \( E_I \) favors the configurations for which the mean cluster distance \( \bar{x} \) is large but \( \bar{x} \) (the intrachurchal particle distance) is small, as will be seen later.

To better display the dependencies, we normalize both the sum in Eq. (8) (which scales as \( \sim n^2 \)) and the degeneracy, \( g^{\nu} \), introducing \( \tilde{g}^{\nu} = g^{\nu}/n \). Considering the previous relation between \( n \) and \( \bar{x} \), and combining Eq. (6) and Eq. (8):
\[
\frac{E(\bar{x}, \bar{z})}{N} = \epsilon_0 \frac{\bar{x}^2}{\chi} + \epsilon_h \gamma C \left( \frac{r_0}{\bar{x}} \right)^{b} + \epsilon_n \frac{\bar{x}^2}{9} \frac{\gamma \chi}{n^2} \sum_{\mu_{h},\mu_{b}=1}^{2n-1} \tilde{g}^{\mu_{h}} \tilde{g}^{\mu_{b}} e^{-((\bar{x} + (\mu_{h} + \mu_{b} - 2n) \bar{z})/R)}^{b}. \tag{9}
\]

Eq. (9) is our main analytical result. It contains three terms, which help us to understand the different effects giving rise to the crystal cluster-crystal phase arising at very low temperatures. The first term describes the tendency of the soft potential to favor clusters as close as possible (small \( \bar{x} \)), simply because in this way, at constant mean density \( \rho_0 \), each cluster would be less populated and the internal repulsion will be smaller. This tendency is opposed by the third term, which comes also from the soft potential, and contains coupled geometric contributions from both \( \bar{x} \) and \( \bar{z} \). With respect to the \( \bar{x} \) dependence, the third term in Eq. (9) is approximately \( \propto \bar{x}^{2} \exp(- (\bar{z}/R)^{b}) \), if we neglect the weak influence of \( \bar{z} \). The intermediate between this dependence of the third term and the \( \bar{x}^{2} \) dependence of the first one singles out two values of \( \bar{x} \) by energy minimization: \( x_m = 0 \) and \( x_c > R \). The first one, and in general the values coming from Eq. (9) for \( \bar{x} < R \), are not reliable within the approximations used: when \( \bar{x} < R \) interactions with clusters beyond nearest neighbors would need to be taken into account, which would raise the energy. Also, the condition of having a cluster lattice without empty clusters implies \( \bar{x} \geq t \approx L/\sqrt{N} \). Indeed if \( \bar{x} = t \) the clusters have population equal to one (\( N_c = 1 \)) and the cluster self-energy is equal to zero and thus exploring \( \bar{x} \) below this
Theoretical results of the previous section are approximately valid only in the limit of vanishing temperature. At finite temperature, energy minimization should be replaced by free-energy minimization, which requires limit is meaningless. Thus, neglecting the behavior for $x < R$, the interplay between the first and third terms selects at zero temperature an equilibrium value $x > R$ which we call $x_c$ (see Fig. 4 (a) and (c)). $x_c$ is nearly insensitive to the value of $x$.

The second term in Eq. (9) arises from the hard-core potential and simply expresses that this short-range repulsion favors large $x$. Again, the third term balances this tendency since larger $x$ imply that some particles of different clusters come closer (the particles such that $\mu_a + \mu_b - 2n < 0$), which is unfavorable for the soft-core intercluster repulsion. The balance between the two tendencies determines the zero-temperature equilibrium value of $x$, which we call $x_c$. Taking into account the $x$-dependence in Eq. (8) is crucial to predict a finite $x_c$.

Indeed, this is the only dependence which can balance the repulsive $1/x^2$ term appearing in the cluster self-energy. We also note that if $\epsilon_h = 0$ all particles in a cluster would collapse to its center ($x = 0$), which is indeed what happens at zero temperature in the absence of the hard-core potential.

In order to check our approximate expression, in Fig. 4 we plot as functions of $R$ and $r_0$ the equilibrium inter-cluster distance, $x_c$, and the equilibrium inter-particle distance inside a cluster, $x_c$, as obtained from numerical simulations of the Brownian set of particles, showing a good agreement with the theoretical prediction from the minimization of our energy expression. In particular, in the case of the intercluster distance (Panel (a) of Fig. 4) we compare the prediction with two different simulation settings, with and without the hard-core potential (purely soft-core potential). As expected, the smaller scale does not influence much the intercluster distance $x_c$, which is quite constant with respect to $r_0$, for $r_0 \ll R$. This confirms, in agreement with [11], that the microscopic details of the clusters are macroscopically less relevant. The relevance of the small-scale appears in determining the intracuster distance $x_c$ (Fig. 4 panel (b)), which depends strongly on $r_0$, and so the average size of the clusters (which is roughly $x_c \sqrt{N_c}$).

The panel (c) of Fig. 4 plots $E(x, \hat{x} = x_c)$ as a function of the intercluster distance $\hat{x}$ for parameters $\gamma$ and $\gamma_f$ corresponding to two different cluster lattices (hexagonal and square). It is seen that the hexagonal minimum is lower (remember than the minimum at $\hat{x} = 0$ and the whole regime $\hat{x} < R$ should be disregarded as Eq. (9) is not valid there), implying that the hexagonal cluster crystal is the most stable. Similar results appear in [12] for the hard-core/soft-shoulder potential in the context of the lattice description.

IV. FINITE TEMPERATURE CORRECTIONS

The theoretical results of the previous section are approximately valid only in the limit of vanishing temperature. At finite temperature, energy minimization should be replaced by free-energy minimization, which requires to take into account the role of the entropy, $S$. Approaches in this line for the lattice shoulder potential can be found in [11, 12]. In this Section, we estimate the free energy and use it to characterize temperature effects on the cluster structure.

In principle, we can distinguish between different entropic sources: the inter-cluster entropy, $S_I$, which takes into account the defects of the cluster-crystal lattice, and the internal entropy of the clusters, $S_C$. In general, $S_I \ll S_C$, if $N_C \gg 1$ since, roughly, $S_I \propto n_c = N/N_c$ and $S_C \propto N$. For this reason, we focus on the calculation of $S_C \approx S$, which strongly depends on the intracuster regime we are considering. Below, we compute it in the crystal cluster-crystal and in the fluid (gas-like) cluster-crystal phases, where we developed reasonable ap-
proximations for the probability distribution of the particle positions. In an intermediate liquid cluster-crystal regime, the situation is different since all the intra-cluster particles have positions correlated in a non-trivial way, as usual in the framework of liquid theory. We point out that in the fluid cluster-crystal regime $S_C$ plays a fundamental role in determining the average size of the cluster, in agreement with [10] for purely soft-core potentials.

A. Very low temperature: Crystal cluster-crystal phase

We consider first the situation of very low temperature, in which the cluster crystal with crystalline interior remains, and neglect any temperature influence in the positions of the cluster centers (which then remain in a hexagonal lattice of intercluster distance $\hat{x}_c$). In the same way, we assume that particles inside each cluster remain close to the positions in the hexagonal lattice of distance $\hat{x}_c$ which characterizes the zero-temperature equilibrium state. This implies neglecting any thermal dilation effect which could affect $\hat{x}_c$ or $\hat{x}_c$. The only temperature effect we estimate now is the possible vibration of each particle around its equilibrium position, characterized by a width $\sigma_h$. To this end, we concentrate on the vibrational entropy $S_v$, neglecting any translational entropy associated with the displacement of the equilibrium particle positions, which will eventually favor the formation of defects.

We make a further mean-field-like approximation in order to evaluate $S_v$: interactions among particles are already taken into account in determining the lattice constants $\hat{x}_c$ and $\hat{x}_c$ and we neglect any further effect in producing particle-position correlations. More specifically, we assume the $N$-particle probability of positions to factorize: $P_N(x_1, ..., x_N) = \prod_{i=1}^{n_c} \prod_{i=1}^{N_c} p(x_i - \hat{u}_s)$, where the first product runs over the $n_c$ clusters and the second over $\{\hat{u}_s\}$, the (zero-temperature) equilibrium positions of the particles. $p(x)$ gives the probability distribution of the position fluctuations of each particle around its equilibrium. We consider the same $p(x)$ for each particle, independently of its position in the cluster. Then, the entropy associated to $P_N$ becomes a sum of terms, one for each particle:

$$S_v = n_c N_c S_1, \quad S_1 = -k_B \int d\mathbf{x} p(\mathbf{x}) \log p(\mathbf{x})/\rho_0.$$

(10)

Our strong-localization assumption implies that no combinatorial factor coming from indistinguishability needs to be used. Our final assumption is that at very low temperatures $p(x)$ is a narrow two-dimensional Gaussian of width $\sigma_h$ [20], so that:

$$S_v = -k_B n_c N_c \int d\mathbf{x} e^{-\mathbf{x}^2/2\sigma_h^2} \log \left( e^{-\mathbf{x}^2/2\sigma_h^2} \right)$$

$$= k_B n_c N_c \left( 1 + \log(2\pi) + \log(\sigma_h^2/\rho_0) \right).$$

(11)

We have used that for a two-dimensional isotropic Gaussian variable, $\langle x^2 \rangle = \langle x^2 \rangle + \langle y^2 \rangle = 2\sigma_h^2$. The width $\sigma_h$ is the only remaining parameter and will be determined from the minimization of the free-energy. To be consistent with the approximations used, the resulting width should satisfy $\sigma_h \ll \hat{x}$.

Next, we evaluate the average energy of the system, separated in intrachannel and interchannel interactions:

$$\langle E \rangle = \langle E_C \rangle + \langle E_I \rangle$$

$$= \sum_{a=1}^{n_c} \sum_{i<j}^{N_c} d\mathbf{x}_i \mathbf{y} N \langle x_i - x_j \rangle V(x_i - x_j)$$

$$+ \sum_{a=1}^{n_c} \sum_{i<j}^{N_c} \sum_{b=1}^{n_c} \sum_{j<\hat{h}} \sum_{i<j}^{N_c} d\mathbf{x}_i \mathbf{y} N \langle x_i - x_j \rangle V(x_i - x_j).$$

(12)

Under the same approximate mean-field framework as for the entropy, we split $P_N$ into a product of single-particle (Gaussian) probabilities. For the intrachannel part we arrive to:

$$\langle E_C \rangle \approx n_c N_c \int d\mathbf{x}_1 d\mathbf{x}_2 e^{-\mathbf{x}_1^2/2\sigma_h^2} e^{-\mathbf{x}_2^2/2\sigma_h^2} \sum_{\mathbf{z} \neq 0} V(\mathbf{x}_1 - \mathbf{a}_j - \mathbf{x}_2)$$

$$= n_c N_c \int d\mathbf{z} e^{-\mathbf{z}^2/4\sigma_h^2} \sum_{\mathbf{z} \neq 0} V(\mathbf{z} - \mathbf{a}_j).$$

(13)

The sum is over all position vectors $\{\mathbf{a}_j\}$ of the equilibrium positions of the particles inside a cluster (except the one at $\mathbf{a}_0 = \mathbf{0}$, where we have arbitrarily located the equilibrium position of the first particle), which form a hexagonal lattice. The last equality is obtained after changing variables to the average, $\mathbf{u} = (\mathbf{x}_1 + \mathbf{x}_2)/2$, and relative, $\mathbf{z} = \mathbf{x}_1 - \mathbf{x}_2$, coordinates, and integrating over $\mathbf{u}$.

The interaction potential is made of the hard-core and the soft-core parts, $V(\mathbf{x}) = V_h(|\mathbf{x}|) + V_s(|\mathbf{x}|)$. Since the Gaussian restricts the integration to a region of size $\sigma_h$ around the origin, and we are assuming $\hat{x}_c \gg \sigma_h$, the soft-core potential is effectively constant inside the integral, $V_s(|\mathbf{x}|) = \epsilon_s (1 + \mathcal{O}(\sigma_h/R)^2)$ and then $\sum_{\mathbf{z} \neq 0} V_s(\mathbf{z} - \mathbf{a}_j) \approx (N_c - 1) \epsilon_s$. For the hard-core potential we approximate the interaction sum by the contribution from the nearest neighbors of the particle at the origin, which are at the corners of a hexagon ($\mathbf{a}_1, ..., \mathbf{a}_6$, with $|\mathbf{a}_i| = \hat{x}_c$) (see upper right panel of Fig. 2). Expanding the interaction sum in the vicinity of $\mathbf{z} = \mathbf{0}$:

$$\sum_{i=1}^{6} V_h(|\mathbf{z} - \mathbf{a}_i|) \approx 6 V_h(\hat{x}_c) + 3 \left( \frac{V_h(\hat{x}_c)'}{\hat{x}_c} \right) \mathbf{z}^2 + ...$$

(14)

The terms neglected are of order $\mathbf{z}_x^2$, $\mathbf{z}_y^2$ and $\mathbf{z}_x^2 \mathbf{z}_y^2$, and thus will give corrections smaller than $(\sigma_h/\hat{x}_c)^2$. Intro-
Introducing in Eq. (13) and performing the integration:

$$
\langle E_C \rangle \approx \frac{N_c}{2} \left( (N_c - 1) \epsilon_c + 6V_h(\hat{x}_c) + 6 \left( V_h(x_c) - \frac{V_h(\hat{x}_c)}{\hat{x}_c} \right) \sigma_h^2 \right)
$$

(15)

Considering now the intrACLuster part of the mean energy, we again factorize the N-particle probability. In the previous section, the contribution of the particle positions inside the cluster to $\langle E_I \rangle$ was needed to properly determine the interparticle distance $\hat{x}$. But here, once we take this as fixed, we estimate the temperature corrections to $\langle E_I \rangle$ by assuming that all particle equilibrium positions are at the center of the cluster they belong. Under this approximation:

$$
\langle E_I \rangle \approx \frac{N_c^2}{2} \int dx_1 dx_2 \frac{e^{-\epsilon_c^2/2\sigma_h^2} - e^{-\epsilon_c^2/2\sigma_h^2}}{2\pi \sigma_h^2} \sum_{\bar{b} \neq 0} \langle x_1 - \bar{b} - x_2 \rangle.
$$

The sum is now over all position vectors \{\bar{b}\} of the cluster centers (except the one we arbitrarily locate at \(\bar{b} = 0\), which form again a hexagonal lattice.

Since $r_0 \ll \hat{x}_c = \min_{\bar{b} \neq 0} \langle \bar{b} \rangle$, the contribution of the hard-core potential to $\langle E_I \rangle$ is negligible. As before, except for corrections which are $O(\sigma_h / \bar{b})^2$ the soft-core potential in each term of the sum can be considered constant inside the integral. Restricting the sum to the six clusters surrounding (at distance $\hat{x}_c$) the one at the origin, we find:

$$
\langle E_I \rangle \approx \frac{N_c^2}{2} 6V_s(\hat{x}_c).
$$

(16)

We can now write the full expression for the free energy:

$$
\begin{align*}
F &= \frac{\langle E \rangle - TS}{n_cN_c} \\
&= \frac{E_0}{n_cN_c} - D(1 + \log(2\pi)) + 3 \left( V_h(\hat{x}_c) + \frac{V_h(\hat{x}_c)}{\hat{x}_c} \right) \sigma_h^2 - D \log(\sigma_h^2/\rho_0).
\end{align*}
$$

(18)

Where we have used $D = k_B T$, and we have collected all terms of the mean energy which are independent of $\sigma_h$ into the constant $E_0$. By minimizing with respect to $\sigma_h$ and taking the explicit forms for $V_s$ and $V_h$ we find:

$$
\sigma_h^2 = \frac{D}{3} \left( 1 + \frac{V_h(\hat{x}_c) + V_h(\hat{x}_c)}{\hat{x}_c} \right) = \frac{2\epsilon_h(\hat{x}_c)^3}{3V_h(\hat{x}_c)}
$$

(19)

which is the expression characterizing the influence of temperature on the fluctuations of each particle position around its equilibrium location. Note that this is precisely the expression for the standard deviation of the Gaussian probability which describes the motion of a Brownian particle in the harmonic approximation, close to the origin, due to the combined potential of six particles at hexagonal positions surrounding the origin at distance $\hat{x}_c$. The consistency condition $\sigma_h \ll \hat{x}_c$ implies that Eq. (19) is only valid at small temperatures such that $D \ll D_h = 3\epsilon_h(x_0/\hat{x}_c)^3$. One may think that $D_h$ gives a rough estimation of the transition temperature above which the crystalline structure inside the clusters is lost (probably into a liquid-like phase), but we think it is at best a rough upper bound, because of the many approximations involved. In a liquid-like phase particles do not fluctuate around any equilibrium points. Moreover, the dynamics is correlated meaning that the main hypothesis of our calculation is not satisfied. Minimizing Eq. (18) also with respect to the intra- and intercluster distances we can obtain entropic corrections to them. These corrections are $O(D)$ and therefore very small in this phase.

B. Fluid cluster-crystal phase

Numerical simulations indicate that there is a range of temperatures in which clusters remain but particles inside them do not display a crystal structure, but a fluid-like behavior. This implies that thermal motion inside the cluster has exceeded the capacity of the hard-core potential to keep the particles in place, as it would occur if $D \gtrsim D_h$. Because of this, and since we know that clusters appear because of the nature of the soft-core repulsion (forming a large hexagonal lattice with lattice vectors \{\bar{b}\}), we describe this fluid-cluster crystal state by completely neglecting the hard-core potential, i.e. $V(\bar{x}) \approx V_s(|\bar{x}|)$. In this gas-like situation, we now estimate how the cluster width $\sigma_s$ depends on temperature.

In the same mean-field approach as before, we consider that the many-body probability, $P_N$, factorizes into single-particle Gaussians - but this time of width $\sigma_s$ - characterizing cluster size, since each particle can explore the whole cluster in the fluid state. A consistency condition is that $\sigma_s \ll \hat{x}_c$ for the crystal-cluster structure to remain despite the finite size of the clusters. In fact, we should also have $\hat{x}_c \sqrt{N_c} \ll \sigma_s$, since the first term is an estimation of the size of a cluster of $N_c$ particles in the low-temperature regime within which it retains a crystal structure. Similarly to the previous low-temperature case (see Eq. (11)), the vibrational entropy will be:

$$
S_v = k_B n_c N_c \left( 1 + \log(2\pi) + \log(\sigma_s^2/\rho_0) \right).
$$

(20)

For the mean energy, we distinguish again the cluster self-energy ($E_C$) and the intercluster contribution ($E_I$). For this last quantity, we introduce the probability factorization into Eq. (10) to obtain (c.f. Eq. (16)):

$$
\langle E_I \rangle \approx \frac{n_c N_c^2}{2} \int dx_1 dx_2 \frac{e^{-\epsilon_c^2/2\sigma_s^2} - e^{-\epsilon_c^2/2\sigma_s^2}}{2\pi \sigma_s^2} \sum_{b=1}^6 V_s(|x_1 - b - x_2|).
$$

(21)
We have approximated all equilibrium particle positions as located at the center of the cluster they belong, and interactions have been restricted to the six clusters (with \( b_i = \hat{x}_c \)) neighboring the first one, which we have arbitrarily located at the origin. The last equality is obtained after transforming to relative and center-of-mass coordinates and integrating over the last one. Using the expansion (c.f. Eq. (14))

\[
\sum_{b=1}^{6} V_s(\mathbf{z} - b_i) \approx 6 V_s(\bar{x}_c) + \frac{3}{2} \left( V_s(\bar{x}_c)'' + \frac{V_s(\bar{x}_c)'}{\bar{x}_c} \right) \mathbf{z}^2 + \ldots ,
\]

we obtain:

\[
\langle E_I \rangle \approx 3 n_c N_c^2 \left( V_s(\bar{x}_c) + \left( V_s(\bar{x}_c)'' + \frac{V_s(\bar{x}_c)'}{\bar{x}_c} \right) \sigma_s^2 \right). \tag{23}
\]

The intrachannel self-energy reads:

\[
\langle E_C \rangle \approx n_c \frac{N_c(N_c - 1)}{2} \int dx_1 dx_2 e^{-x_1^2 / 2\sigma_s^2} e^{-x_2^2 / 2\sigma_s^2} \sum_{j \neq 1}^{N_c} V_s(\mathbf{x}_1 - \mathbf{x}_j) + n_c N_c \int dz e^{-x^2 / 4\sigma_s^2} V_s(|z|). \tag{24}
\]

For the GEM-\( \alpha \) potential, \( V_s(|z|) = \epsilon_s(1 + O(|z/R|^\alpha)) \), being the last term negligible, if \( \alpha > 2 \), compared to the terms already considered in Eq. (22). This is precisely the reason why cluster crystals form in a GEM-\( \alpha \) potential with \( \alpha > 2 \); the particle repulsion inside the cluster is negligible compared with the repulsion from the neighboring clusters [10]. Thus, neglecting terms smaller than \( \mathcal{O}(\sigma_s/R^2) \):

\[
\langle E_C \rangle \approx n_c \frac{N_c(N_c - 1)}{2} \epsilon_s. \tag{25}
\]

The complete expression for the free energy in this fluid or gas cluster regime is:

\[
\frac{F}{n_c N_c} = \frac{(E) - TS}{n_c N_c} \approx \frac{\bar{E}_0}{n_c N_c} - D(1 + \log(2\pi)) + 3 N_c \left( V_s(\bar{x}_c)'' + \frac{V_s(\bar{x}_c)'}{\bar{x}_c} \right) \sigma_s^2 - D \log(\sigma_s^2 \rho_0). \tag{26}
\]

All terms of the mean energy which are independent of \( \sigma_s \), have been included in \( \bar{E}_0 \). Minimizing with respect to \( \sigma_s \), and taking our explicit expression for \( V_s \) gives:

\[
\sigma_s^2 = \frac{D}{3 N_c \left( V_s(\bar{x}_c)'' + \frac{V_s(\bar{x}_c)'}{\bar{x}_c} \right)} - \frac{D \bar{x}_c^2 e^{\epsilon_s(\alpha)} (R/\bar{x}_c)^\alpha}{3 \alpha^2 \epsilon_s N_c ((\bar{x}_c/R)^\alpha - 1)}. \tag{27}
\]

As in Eq. (19), this is the width of the Gaussian probability distribution for a Brownian particle moving in the combined potential of six clusters located on the corners of a hexagon at distance \( \bar{x}_c \) from the origin, each providing a repulsion given by the potential \( N_c V_s \), and under the harmonic approximation close to the origin. It also coincides, after noting that the number of particles in each cluster of a hexagonal cluster crystal is \( N_c = \rho_0 \sqrt{3 \bar{x}_c^2 / 2} \), with the cluster width derived from approximations to the Dean-Kawasaki equation in a GEM-\( \alpha \) potential [10]. We recall that expression (27) is expected to be valid only in the intermediate temperature range such that \( \bar{x}_c \sqrt{N_c} \ll \sigma_s \ll \bar{x}_c \). Violation of the last inequality, i.e. \( \sigma_s \approx \bar{x}_c \), gives a rough upper limit to the melting temperature of the cluster crystal. The results in [10] indicate that indeed this estimation overestimates the cluster crystal melting temperature (for the system in which only the interaction \( V_s \) is present) although the qualitative parameter dependence is correct. As a final remark, minimizing Eq. (26) with respect to the inter-cluster distance would allow us to estimate the temperature corrections in determining \( \bar{x}_c \). These corrections are all \( \mathcal{O}(D) \).

V. SUMMARY AND DISCUSSION

We have studied the influence of a hard-core potential on the cluster crystal phase of a system of particles interacting through a GEM-\( \alpha \) repulsive potential. Performing off-lattice numerical simulations of the interacting Brownian particles we have identified the different ordering types that particles inside the clusters exhibit. Temperature drives a transition from a crystal cluster-crystal scenario (where particles within clusters are periodically ordered) to a fluid/gas cluster-crystal one. In the small temperature limit, an energy expression has been obtained which helps to understand the balances between the different forces leading to the existence of the cluster-crystal phase. In addition, the finite temperature value of the cluster width has been obtained for the fluid cluster-crystal state, and also for the fluctuation amplitude of the particles around their equilibrium positions in the crystal cluster-crystal state. They provide rough upper limits to the temperatures at which transitions would take place.

The methodology employed is rather general, and other types of potentials, leading to cluster crystals, could be considered. See for instance the soft potential in [21, 22] in the context of bosonic interactions. Furthermore, we expect our approach to be of use to describe biological aggregations in which the individuals have a finite size and interact through forces acting attractively and/or repulsively at different scales or through competing/mutualistic dynamics [23]. The generalization of our study to non-equilibrium systems of particles with finite-size and interacting through repulsive forces is of much interest in the context of active matter and will be considered in the future, extending approaches such as those in Ref. [24].
VI. ACKNOWLEDGEMENTS

We acknowledge financial support from the Spanish grants LAOP CTM2015-66407-P (AEI/FEDER, EU) and ESOTECOS FIS2015-63628-C2-1-R (AEI/FEDER, EU). We acknowledge fruitful discussions and continuous support from Profs. Umberto Marini Bettolo Marconi and Angelo Vulpiani.