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Multiple occupancy crystals formed by purely repulsive soft particles

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Abstract
Recently, particular interest has been placed in the study of a strikingly counter-intuitive phenomenon: the clustering of purely repulsive soft particles. This contribution serves the purpose of both reviewing our current understanding of the multiple occupancy crystals and presenting details of recently developed tailor-cut approaches to the problem. We first indicate, by use of analytically tractable examples, how such a phenomenon can arise at all. We then show that the thermodynamic formalism has to be adapted when studying such systems and present a novel computer simulation technique apt to do so. Finally, we discuss the intriguing mechanical and structural responses of such systems upon increasing the density.

1. Introduction

As a rule-of-thumb, we can define soft matter as most substances that, due to air travel regulations, are nowadays only allowed to be carried in one's hand baggage if they are stored in containers of up to 100 ml and placed in a transparent re-sealable plastic bag. Among these we find gels, lotions, pastes, foams, sprays and most complex liquids, placing soft matter everywhere in our everyday lives. This omnipresence fuels the interest of scientists to study the properties and the behavior of such substances. In the present paper, we will focus on a particular class of soft matter systems: suspensions of mesoscopic particles (ranging in size from 1 nm to 1 μm) immersed in a solvent formed by particles of atomic size.

The typically huge number of constituents that build up the mesoscopic particles is one of the key problems in theoretical investigations of soft matter systems. It is not feasible to use concepts based on statistical mechanics that are able to take all the degrees of freedom of these building particles explicitly into account. It is therefore more appropriate to focus rather on a simplified representation of the interaction between two macromolecules which may be obtained by applying suitable coarse-graining procedures [1, 2]. These techniques average over many internal and solvent molecular degrees of freedom, leading to *effective* particles, but leaving the thermodynamic properties of the system unchanged. These effective particles are then identified by a set of simplified characteristics, such as their center-of-mass position, relative orientation or spatial extent, i.e. the radius of gyration. The interaction between two such effective particles is modeled by an effective pair potential. For a few colloidal dispersions such effective interactions have been proposed or derived in the literature, sometimes even in closed, analytical form: neutral [3] and charged [4, 5] star polymers as well as microgels [6–9] are a few examples. For an overview we refer to [2].

In the special case of polymeric macromolecules of low inner monomer concentration, such as polymer chains [10–12], dendrimers [13, 14], microgels [6–9] or diblock copolymers [15, 16], it is conceivable that—as a consequence of their internal structure—these effective particles may overlap, mutually penetrate or even intertwine when compressed. The centers of mass of two such macromolecules might even coincide as long as their constituent monomers do not

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overlap and still obey the excluded-volume conditions at the microscopic level. Thus, since full overlaps between the *effective* particles are possible, the resulting effective interaction remains finite, i.e. bounded, at zero separation. In striking contrast to the simple, harshly repulsive interatomic potentials typically known from atomic systems, the effective potentials characteristic of soft matter systems lead to completely new features and a considerably richer variety of ordered phases. Among those are not only the face-centered cubic arrangement assumed by colloidal spheres at high concentrations [17–19] and low-symmetry crystals formed by soft spheres [20, 21], but also a variety of periodic assemblies observed for charged colloidal mixtures [22] as well as the gyroid and other microphases of diblock copolymer solutions [23–25].

In this work we will concentrate on a novel and undoubtedly counter-intuitive form of self-assembly in soft matter that was recently predicted: the formation of clusters in systems interacting by soft, purely repulsive effective potentials, i.e. the formation of aggregates of particles which organize themselves into regular crystals with multiple site occupancy [26, 27].

This paper is organized as follows: in section 2 we present the most prominent models of bounded, purely repulsive interactions and discuss their different phase behaviors. One of these scenarios is the aforementioned clustering phenomenon. In section 3, we motivate how purely repulsive particles can agglomerate. Section 4 is dedicated to a detailed study of the thermodynamic formalism governing clustering systems and its consequences in computer simulations. The particular case of the mechanical properties of these systems will also be considered. We summarize and conclude in section 5.

2. Models

Arguably the best-studied model of bounded interaction is the Flory–Krigbaum potential, proposed in the pioneering work of its authors given in 1950 [28]. This Gaussian-like potential was put forward as an effective interaction between polymer chains. In the mid-1970s, the statistical mechanics of many-body systems of particles interacting by Gaussian potentials became the subject of a series of seminal papers by Stillinger and coworkers [29–33]. The Flory–Krigbaum–Stillinger model has thus become one of the most prominent models in the class of bounded, purely repulsive interactions. It is now commonly known as the Gaussian core model (GCM) and defined by

$$\phi_{\mathrm{GCM}}(r) = \varepsilon \exp[-(r/\sigma)^2], \qquad (1)$$

where ε and σ denote the energy and length scale, respectively. Whereas Stillinger's early work mainly concerned mathematical properties of the system, such as duality relations between real and reciprocal space and virial expansions [29–33], later on the thermodynamics and phase behavior took center stage [34–37] and very recently attention has turned to the phonon spectra of the GCM in equilibrium and shear crystals [38]. Concerning the phase diagram of the GCM, it has been found [34, 35, 37] that, at high temperatures T, the fluid phase is stable at all densities, while at sufficiently low T compressing a GCM fluid leads via a first-order phase transition to a cubic phase with singly occupied lattice sites. Upon further compression, the crystal might undergo a structural phase transition but eventually melts anew [34, 35, 37]. This behavior is called *re-entrant melting*.

Are there physical systems that realize the GCM as an effective interaction? Due to a series of theoretical and simulation studies [10–12, 39–46], the question can be answered in the affirmative. Indeed, the GCM allows for an accurate description of the interactions of a *pair* of polymer coils in *good solvents*. Still, the question remains: how *realistic* is such an interaction for *dense* polymer chain systems or for other colloidal systems? To this end, recent work has provided further support for the validity of the GCM. Louis *et al* [12] calculated the effective pair potential for systems containing hundreds of polymer chains, covering a broad range of concentrations ranging from dilute solutions up to several times the overlap concentration. The study confirmed the validity of the Gaussian-like pair interaction for this system for the whole concentration range, with only slight modifications of the length and energy scales beyond the overlap concentration [12]. A way to avoid the density dependence of the potential was furthermore offered by the recent 'multiblob' approach of Pierleoni *et al* [47]. Other soft matter systems such as microgels [6, 7] or dendrimers [13, 48] were also shown to interact via Gaussian-shaped effective potentials. For the latter case, similar results to those presented by Louis *et al* in [12] were obtained for the study of dense dendrimer systems [49]. Moreover, the theoretical predictions for the shape of the effective interaction of such dendrimers are also in very good agreement with results from small-angle neutron scattering experiments [48], which provides confidence that the GCM is indeed a realistic model for the effective interactions between various polymeric macromolecules.

Another member of the family of bounded interactions is the penetrable sphere model (PSM), defined by the pair potential

$$\phi_{\mathrm{PSM}}(r) = \begin{cases} \varepsilon & r < \sigma \\ 0 & \text{else}. \end{cases} \qquad (2)$$

The PSM has also been extensively studied recently [50–60]. Surprisingly, its phase behavior is markedly different from that of the GCM. For all T, increasing the density of a PSM fluid leads to the formation of clusters of overlapping particles arranged in an ordered phase. So far, this clustering phenomenon has not been observed in experiments or in monomer-resolved simulations of soft matter systems, but recent predictions by some of us [61] might change this state of affairs. The assembly of pairs of *amphiphilic* dendrimers *in silico* leads to effective interactions that are intermediate between the GCM and the PSM. Compared to the GCM, these potentials show steeper flanks as well as flatter regions or even a dip at small separations. As we will argue in the following section, these interactions fall in the clustering class of potentials. Amphiphilic dendrimers could thus show clustering behavior under appropriate conditions.

3. Motivation

The above considerations and results raise the following questions: how can particles that are purely *repulsive* actually *agglomerate* in stable clusters and freeze into crystalline assemblies? Furthermore, what is the qualitative difference between the GCM and the PSM that is responsible for their distinctly different phase behaviors? The following sections sketch answers to these questions.

3.1. From re-entrance to clustering

As an intuitive motivation for the existence of different types of phase behavior depending on the nature of the bounded interaction, let us consider a one-dimensional array of particles separated by a fixed distance a and interacting via some bounded, purely repulsive potential. Though the arguments put forward in the following also hold in higher dimensions, this choice makes the argument easier to visualize [62]. The sum of the pair interactions forms the potential energy landscape that a test particle inserted into this system would feel. In the case of Gaussian interactions, we see in the upper row of figure 1 that the resulting potential energy landscape has minima in between the particles of the lattice, thereby suggesting that the preferred location of the additional particle would destroy the periodicity. However, if we change the interaction potential slightly by making it steeper at its flank and flatter for small separations, we obtain a distinctively different scenario (cf lower row of figure 1). Now, the potential energy *maxima* form in between the particles. This would therefore drive the test particle to sit precisely *on top* of one of the particles of the system. The position of the test particle is thus compatible with the lattice structure, suggesting that clustering is preferred by this system. Note that the test particle itself interacts with all other particles and thereby modifies the energy surface, so this argument has to be treated with some care, but it is nonetheless qualitatively correct.

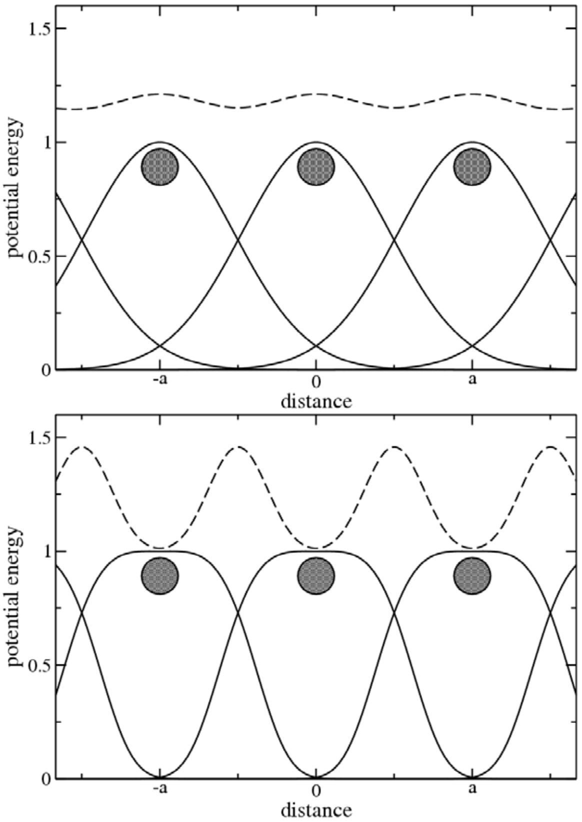

Figure 1. The interactions (solid line) of a one-dimensional array of GCM particles (gray circles) sum up to an effective potential energy landscape (dashed line) felt by a test particle (upper row). As can be seen, minima have formed in between the location of the particles. Thus an additional particle will destroy the regular spacing. In the lower row, the same is shown for particles interacting via $\phi(r) = \varepsilon\exp[-(r/\sigma)^4]$, which has a flatter core region and a slightly steeper flank than the GCM. Now, energetic minima of the collective energy landscape have formed at the positions of particles, allowing a test particle to sit on top of a lattice point, thereby causing the system to cluster.

3.2. From fluid to multiply occupied crystal

It has to be stressed that the above discussion is based on purely energetic arguments and neglects entropy. But since the role of entropy in this problem is mainly to set the precise location of the phase transition, this does not alter the ground state ordering at high densities. To demonstrate this let us examine a simple model for the free energy. For simplicity, we consider the two-dimensional analog of the PSM, i.e. penetrable discs, where an overlap between two discs results in an energy penalty of ε. Again, our argument is independent of dimension, but this choice makes a visualization of the system easier. By making use of Widom's particle insertion method, we first approximate the free energy of a *liquid* consisting of penetrable particles. In particular, we assume that, upon random insertion of a particle in a uniform, dense fluid, the number of overlaps n_{fl} with the particles of the system is large, i.e. $n_{\mathrm{fl}} \gg 1$, and that we may therefore ignore its fluctuations. The excess chemical potential μ^{ex} is then equal to the energy change $\Delta\Phi$ upon inserting an additional disc:

$$\mu^{\mathrm{ex}} = \Delta\Phi = n_{\mathrm{fl}}\varepsilon = \pi\rho\sigma^2\varepsilon. \tag{3}$$

The free energy per particle of the fluid phase f_{fl} is obtained by adding the ideal gas contribution to $\mu^{\mathrm{ex}}/2$:

$$f_{\mathrm{fl}}(\rho, T) = k_{\mathrm{B}}T\left[\ln(\rho\Lambda^2) - 1\right] + \tfrac{1}{2}\pi\rho\sigma^2\varepsilon. \tag{4}$$

Here, k_{B} is Boltzmann's constant and Λ denotes the de Broglie wavelength.

Inspired by the study of hard discs [63, 64], we calculate the free energy of a *clustered solid* within a cell model. Assuming that the system wants to freeze in a close-packed structure, i.e. a triangular lattice with lattice constant a (cf figure 2), the number of particles n_{c} that occupy a single lattice site is

$$n_{\mathrm{c}} = \frac{\sqrt{3}\rho a^2}{2}. \tag{5}$$

Here again we consider the high density limit where $n_{\mathrm{c}} \gg 1$. Moreover, we assume that, besides confining each other to the vicinity of their lattice sites, the particles in neighboring boxes do not interact and then, as can be gathered from figure 2, the

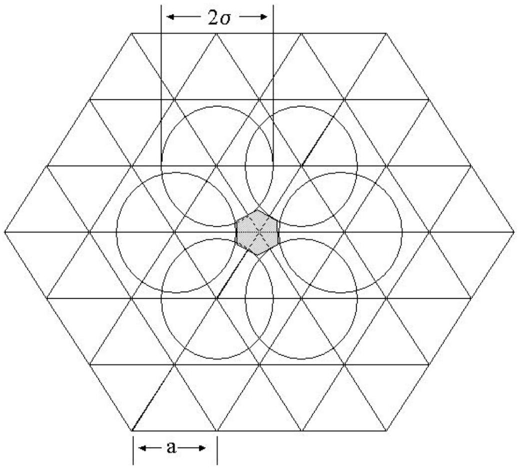

Figure 2. Crystalline penetrable discs (diameter σ) confine each other to the vicinity of their lattice sites, which can be visualized by plotting the corresponding exclusion discs (radius σ). The area accessible to the center of a test disc (shaded gray) in the middle of the figure is bounded by the areas excluded by the surrounding exclusion discs (the central disc itself is not shown).

free space available to the *centers* of the particles is limited to a small area approximately given by

$$A_{\text{free}} \approx 2\sqrt{3}(a-\sigma)^2. \tag{6}$$

Then, the ideal contribution to the free energy per particle is

$$f_{\text{sol}}^{\text{id}}(\rho,T) \approx k_B T\left[\ln(n_c\Lambda^2/A_{\text{free}})-1\right] = k_B T\left\{\ln\left[\frac{\rho a^2\Lambda^2}{4(a-\sigma)^2}\right]-1\right\}. \tag{7}$$

Since every cell contains n_c particles, the energy per cell equals $\varepsilon n_c(n_c-1)/2$, which amounts to an energy per particle of $\varepsilon(n_c-1)/2$. Using (5), we then obtain the free energy of the solid:

$$f_{\text{sol}}(\rho,T) = k_B T\left\{\ln\left[\frac{\rho a^2\Lambda^2}{4(a-\sigma)^2}\right]-1\right\}+\frac{\sqrt{3}\rho a^2-2}{4}\varepsilon. \tag{8}$$

As a tends to σ with increasing density, $(a-\sigma)$ does not vanish exponentially fast, so at high densities the dominating contribution for both the liquid and the cluster solid is the energetic term linear in ρ. Comparing their coefficients for the different phases, we find that $\pi/2 > \sqrt{3}/4$ and therefore the cluster solid phase is more stable at high densities. Obtaining the precise location of the fluid to crystal phase transition would require a more careful analysis, but this argument captures the essence of the underlying physics.

3.3. Cluster criterion

Putting together these toy model results suggests that clustering occurs in the PSM, but not in the GCM, as a consequence of how the pair interaction decays with increasing distance. But which properties of the decay lead to clustering? Based on an analysis of the behavior of the structure factor within the mean field approximation, Likos *et al* [26] established a criterion that allows us to determine whether clustering or re-entrant melting behavior will be observed in systems interacting via bounded, entirely repulsive potentials. The criterion applies for pair interactions $\phi(r)$ that decay to zero sufficiently fast as $r\to\infty$, so that they are integrable and their Fourier transforms exist. There are then two possible scenarios for the functional behavior of the Fourier transform of the pair potential $\widetilde{\phi}(q)$ as a function of the wavenumber q [26].

- If $\widetilde{\phi}(q)$ is a non-negative function, i.e. $\widetilde{\phi}(q) \geqslant 0$ for all q, a system of such particles will show re-entrant melting. Since the Fourier transform of the GCM is of Gaussian shape, it belongs to this category, called Q^+ class.
- Otherwise, if the Fourier transform $\widetilde{\phi}(q)$ oscillates, i.e. it attains negative values for certain ranges of the wavenumber q, the system is expected to display clustering behavior. The PSM is a representative of this category, called $Q^\pm$ class.

Note that bounded pair interactions with shoulders flatter than a Gaussian and also decaying faster than the GCM will typically exhibit clustering. In fact, for the class of generalized exponential models (GEM-n), with $\phi(r) = \varepsilon\exp[-(r/\sigma)^n]$, $n > 0$, the transition from the Q^+ to the $Q^\pm$ class occurs precisely at $n = 2$ [65]. This explains why the effective potentials found for amphiphilic dendrimers also fall into this latter category.

4. Thermodynamics

A clustered solid can be contrasted with a regular, single-occupancy crystal at finite temperatures, where there is always a net, though small, concentration of point defects, i.e. of vacancies and interstitials. Thereby, the number of particles in the system differs from the amount of available lattice sites, but this is often neglected in free energy calculations since it hardly affects the results obtained for such solids. In clustered crystals, however, this difference leads to more than just a mere correction in the free energy because *several* particles can share a single lattice site. In the bulk limit, a system will find its equilibrium occupation per lattice site by making adjustments at surfaces or by forming defect areas. A description of clustered solids through simulation, however, brings about novel methodological challenges. Here, the system is constrained by the use of fixed box geometry and/or fixed amounts of particles as well as the use of periodic boundary conditions, which in combination may prevent the system from relaxing to its equilibrium ground state. To reliably simulate clustered solids, it is therefore essential to determine the *equilibrium* occupation of lattice sites.

Fortunately, a solution can be derived [66] from the study of crystal defects [67]. In any system where the amount of particles N differs from the amount of given lattice sites N_c an infinitesimal change in the constrained Helmholtz free energy F can be written as

$$\mathrm{d}F(\mu_c) = -S(\mu_c)\,\mathrm{d}T - P(\mu_c)\,\mathrm{d}V + \mu(\mu_c)\,\mathrm{d}N + \mu_c\,\mathrm{d}N_c. \tag{9}$$

Here, $\mu_c = (\partial F/\partial N_c)_{N,V,T}$ is the change in free energy associated with the insertion of a lattice site into the system.

Note, however, that since no new degree of freedom has been introduced, μ_c solely acts as a constraint on the other variables. The constrained pressure $P(\mu_c)$ is thus given by

$$P(\mu_c) = -\left(\frac{\partial F}{\partial V}\right)_{N,T,N_c}, \tag{10}$$

while the constrained chemical potential $\mu(\mu_c)$ is

$$\mu(\mu_c) = \left(\frac{\partial F}{\partial N}\right)_{V,T,N_c}. \tag{11}$$

The value of the constraint at equilibrium is set by the need to preserve the extensitivity of the Gibbs free energy G. At constant $P(\mu_c)$ and T

$$G = \mu N + \mu_c N_c, \tag{12}$$

so equilibrium properties are recovered when no work is required to increase the size of a system by an additional lattice site, i.e. $\mu_c = \mu_c[N, V, T, N_c^{\text{eq}}(N, V, T)] = 0$. Here, N_c^{eq} is the equilibrium number of lattice sites corresponding to the choice of N, V and T. It then follows that the equilibrium pressure P is related to the constrained pressure $P(\mu_c)$ via

$$P(N, V, T) = P(\mu_c = 0) = P[N, V, T, N_c^{\text{eq}}(N, V, T)], \tag{13}$$

and in a similar way the equilibrium chemical potential μ is connected to the constrained one via

$$\mu(N, V, T) = \mu(\mu_c = 0) = \mu[N, V, T, N_c^{\text{eq}}(N, V, T)]. \tag{14}$$

These expressions relate the properties of a (small) constrained system to the bulk limit. Note that, in the density functional treatment of this problem [65], the variational free energy $\mathcal{F}[\rho]$ is minimized with respect to the lattice site occupancy n_c, a condition that is formally identical to setting $\mu_c = 0$.

In canonical simulations, the constraint can be tested by rewriting the free energy and solving for

$$\mu_c = \frac{F(\mu_c) + P(\mu_c)V - \mu(\mu_c)N}{N_c}. \tag{15}$$

In an effort to identify the equilibrium states of a clustering system, the locus $\mu_c = 0$ must be found for each state point. At a given N, V, T and N_c, the quantities $F(\mu_c)$, $P(\mu_c)$ and $\mu(\mu_c)$ to be inserted into the right-hand side of (15) may be directly computed from Monte Carlo (MC) simulations using, respectively, thermodynamic integration, the virial equation and Widom's particle insertion method [68]. By iterating this procedure for different N and V, while keeping ρ, N_c and T constant, the equilibrium configuration for the given state point is identified as depicted in figure 3. The virial equation and particle insertion methods are by now standard simulation methodologies, but the thermodynamic integration to obtain $F(\mu_c)$ for this specific system brings in a few subtleties. These, as well as some special physical features of clustering systems, are discussed in the following sections.

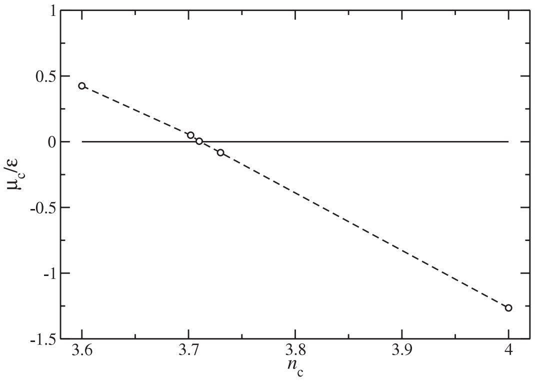

Figure 3. Typical example of Monte Carlo simulation results (circles) for μ_c as a function of the lattice occupation n_c for an fcc solid of particles interacting via $\phi(r) = \varepsilon \exp[-(r/\sigma)^4]$ at state point $k_BT/\varepsilon = 0.2$ and $\rho\sigma^3 = 1.8$. The equilibrium occupation number is identified as the state where $\mu_c = 0$. The dashed line serves as a guide to the eyes.

4.1. Thermodynamic integration for cluster solids

To determine the free energy of solids, Frenkel and Ladd [69] developed a high accuracy technique based on thermodynamic integration [70]. Assuming that the system of interest is governed by the interaction potential $\Phi(\mathbf{r}^N)$, its free energy at a given state point can be related to the known free energy of a reference system F_{ref} interacting via $\Phi_{\text{ref}}(\mathbf{r}^N)$. During the course of the simulations, the system's intermolecular interactions are slowly turned off while the interactions of the reference system are simultaneously turned on. The easiest way to achieve this is to consider the following potential energy function where this process is realized in a linear dependence

$$\Phi_\lambda(\mathbf{r}^N) = (1-\lambda)\Phi(\mathbf{r}^N) + \lambda\Phi_{\text{ref}}(\mathbf{r}^N), \tag{16}$$

with coupling parameter λ. For $\lambda = 1$ the reference system is simulated, while for $\lambda = 0$ the system of interest is recovered. The free energy can then be calculated via

$$F = F_{\text{ref}} + \int_{\lambda=1}^{\lambda=0} \mathrm{d}\lambda \left\langle \frac{\partial \Phi_\lambda}{\partial \lambda} \right\rangle_\lambda. \tag{17}$$

Using (16), this reduces to

$$F = F_{\text{ref}} + \int_{\lambda=1}^{\lambda=0} \mathrm{d}\lambda\, \langle \Phi_{\text{ref}} - \Phi \rangle_\lambda, \tag{18}$$

which expresses the free energy difference as an ensemble average that can be readily measured in MC simulations.

In the original scheme [69], the reference system was an Einstein solid where particles are connected to their respective lattice sites via harmonic springs [68]. This is a reasonable choice for perfect *single*-occupancy crystals. However, in *multiple*-occupancy crystals, not only can several particles be found on a given lattice site, but they can also hop from one lattice site to the next, a property explicitly confirmed in Molecular Dynamics simulations of cluster crystals [71]. In this case ideal gas particles that move in potential wells centered around the lattice sites are a more convenient reference system (cf figure 4). More formally, we set

$$\Phi_{\mathrm{ref}}(\mathbf{r}^N) = \sum_{i=1}^{N} \phi_{\mathrm{ref}}(\mathbf{r}_i), \tag{19}$$

with

$$\phi_{\mathrm{ref}}(\mathbf{r}) = \begin{cases} 0 & \mathbf{r} \in \bigcup_{i=1}^{N_c} v_0(\mathbf{R}_i) \\ U_{\max} & \text{otherwise,} \end{cases} \tag{20}$$

where $U_{\max}$ is the maximal height of the potential barrier and $v_0(\mathbf{R}_i)$ describes a small volume centered around the lattice vector $\mathbf{R}_i$, $i = 1, \ldots, N_c$, of the crystal under study. The free energy calculation does not depend on the size or shape of the volume v_0 as long as these volumes do not overlap and allow us to construct a reversible path to the reference system. For instance, the crystal structure would melt if these regions were too big, so typically the dimensions of v_0 are chosen to roughly fit the width of the cluster density distribution, i.e. the distribution of particles around a lattice site (cf figure 4).

Since the barrier height between the lattice sites is finite ($U_{\max} < \infty$), it is a simple exercise to show that the canonical partition function of the reference system Q_{ref} is given as

$$Q_{\mathrm{ref}} = \frac{1}{\Lambda^{3N} N!} \left(V_0 + V_{\mathrm{barr}} \mathrm{e}^{-\beta U_{\max}} \right)^N , \tag{21}$$

where $V_0 = N_c v_0$ and $V_{\mathrm{barr}} = V - V_0$ is the volume excluded by the barriers. The reference free energy then follows as

$$F_{\mathrm{ref}} = -k_B T \log Q_{\mathrm{ref}}. \tag{22}$$

Apart from the standard MC local particle displacements, two additional trial moves are introduced to avoid sampling problems. At $\lambda = 0$, the barrier is completely turned off and has therefore no influence on the evolution of the system. Still, the barrier enters the formalism in the evaluation of (18). Since the system's center-of-mass motion cannot be restricted as easily as in regular crystals and will randomly fluctuate, particles slowly move on and off the barrier. Therefore, $\langle \partial\Phi_\lambda/\partial\lambda \rangle_{\lambda=0} = \Phi_{\mathrm{ref}} - \Phi$ will change quite drastically during the course of the simulation, resulting in large uncertainties in this quantity. We thus introduce a deliberate random displacement of the system's center of mass. Such moves will almost always be accepted as λ approaches zero because the change in potential energy is minimal, and will thus guarantee a uniform and complete sampling. Another problem is encountered at the other end of the λ range, i.e. for $\lambda \sim 1$. Now, the barrier might be so high that particles cannot cross from one potential well to a neighboring one via standard MC moves. We therefore implement moves where a particle is moved to a completely random position within the simulation box. At $\lambda = 1$, these will be accepted with probability V_0/V.

4.2. Special features: behavior upon increase in density

Since thermodynamic equilibrium is only obtained when $\mu_c = 0$, one might argue that, once the equilibrium points are found, any references to the artificial μ_c field can be discarded. Yet, for second derivatives of the constrained free energy, such as the bulk modulus $B = V(\partial^2 F/\partial V^2)$, μ_c does matter, unless one already has the complete *equilibrium* free energy curve at hand.

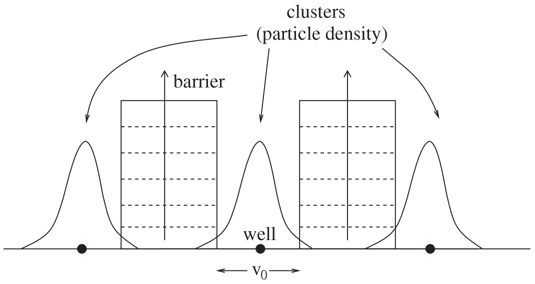

Figure 4. Schematic, one-dimensional representation of the thermodynamic integration scheme for multiple-occupancy crystals. While turning off the interactions of interest, potential wells of increasing height confine the particles to their lattice sites (black circles). The solid curves caricature the density distributions of the clusters.

In single-occupancy crystals, $B = -V(\partial P/\partial V)_{N,T,N_c}$ can be computed directly in simulations [72, 73] for a given state point through

$$B = \frac{2P + \rho k_B T}{3} + \langle \Theta \rangle - \frac{N}{\rho k_B T} \langle \delta(\Pi)^2 \rangle, \tag{23}$$

where

$$\Pi = \rho k_B T - \frac{W}{3V} \tag{24}$$

is the instantaneous pressure with virial W, so $P = \langle \Pi \rangle$. Fluctuations in the pressure are given by $\langle \delta(\Pi)^2 \rangle = \langle \Pi^2 \rangle - \langle \Pi \rangle^2$. The remaining term is complex in general, but reduces to

$$\Theta = \frac{1}{9V} \sum_{i<j} r_{ij}^2 \frac{\partial^2 \phi(r_{ij})}{\partial r_{ij}^2} \tag{25}$$

for pairwise additive interaction potentials $\phi(r_{ij})$, i and j being two particles at distance r_{ij}.

For cluster crystals the artificial system conditions during simulations further modify the bulk modulus. Starting from (13), we write

$$B \equiv -V \left[\frac{\partial P(N, V, T)}{\partial V} \right]_{N,T} = -V \left[\frac{\partial P(\mu_c = 0)}{\partial V} \right]_{N,T} . \tag{26}$$

Differentiating (13) with respect to V we get

$$\begin{aligned} B &= -V \left[\frac{\partial P(\mu_c)}{\partial V} \right]_{N,T,N_c} - V \left[\frac{\partial P(\mu_c)}{\partial N_c} \right]_{N,T,V} \left(\frac{\partial N_c}{\partial V} \right)_{N,T} \\ &= B_{\mathrm{vir}} - B_{\mathrm{del}}, \end{aligned} \tag{27}$$

where the right-hand side is evaluated at $\mu_c = 0$. As we can see from this formula, the system can respond to compression via two different mechanisms that are schematized in figure 5. The first one, expressed by B_{vir}, reflects the behavior that we intuitively expect from a system that is compressed: since the overall volume gets smaller, particles move closer to each other, which leads to affine shrinking of the crystal. The clustering systems under study here, however, also have another mechanism in answer to compression: they can delete

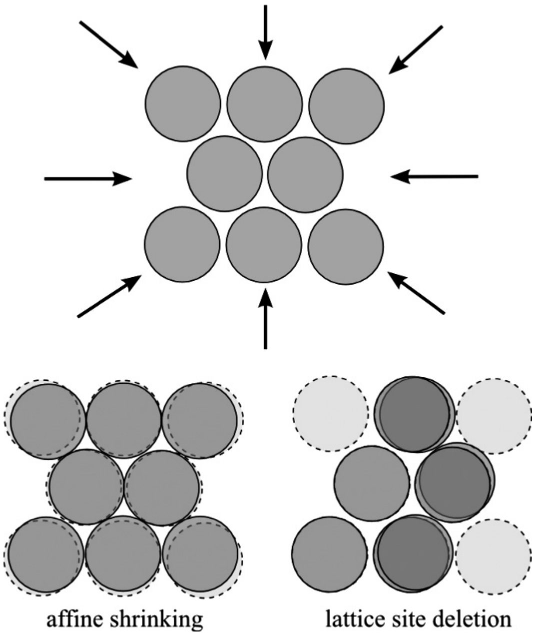

Figure 5. Systems interacting via purely repulsive, bounded interactions that lead to clustering can react to compression via two different mechanisms. On the left-hand side of the bottom panel, particles move closer to each other (at constant number of lattice sites), leading to an affine shrinking of the system. On the right-hand side, lattice sites are deleted and particles redistribute onto the remaining sites.

lattice sites, redistributing the particles from these clusters onto the remaining clusters in the bulk of the crystal. This contribution is captured by B_{del}.

To see which of these two mechanisms is preferred by clustering systems, we determine the bulk modulus by MC simulations for a potential that belongs to the clustering class, i.e. the GEM-4 from the family of potentials introduced above. The bulk modulus B obtained via (27) for the respective stable solids at different temperatures (cf the phase diagram for this system in [66]) is compared in figure 6 to the direct numerical differentiation of the equilibrium (i.e. $\mu_{\mathrm{c}} = 0$) free energy results. A remarkable agreement is obtained between the two approaches. Using (23), we can calculate the affine bulk modulus B_{vir} by itself, which does not capture the lattice site deletion mechanism. It is remarkable that, being far from negligible, the correction to B_{vir} amounts to a reduction of over 40% of its value, as can be seen in figure 6. We therefore see that deletion of lattice sites substantially weakens the response of the system to compression.

This reluctance of clustering systems towards affine shrinking is also reflected in the systems' reaction to an increase in density at *constant* volume. Density functional theory predicts [26, 27, 65] that the equilibrium lattice constant of the crystals shows only small variations and then saturates at high densities. Essentially, the lattice spacing is set by requiring that the shortest reciprocal lattice vectors of the crystal have a magnitude that coincides with q_*, the wavenumber at which $\tilde{\phi}(q)$ attains its negative minimum. Consequently, the equilibrium lattice site occupation for all clustering systems should scale linearly with density, i.e.

$$n_{\mathrm{c}} = c\rho\sigma^3, \tag{28}$$

where c is a constant that is only determined by the details of the interaction potential [65]. Let us assume that this equation were strictly fulfilled. When we then increase the density of a clustering system via addition of particles while keeping the volume fixed, the particles distribute on existing clusters *without* changing either the underlying crystal structure[6] or the volume of a primitive unit cell $v_{\mathrm{c}} = N_{\mathrm{c}}/V$. Simulations confirm that this density functional theory result is asymptotically true for high densities. But at all densities, the volume of a primitive cell changes relatively little (cf figure 7). As a final remark, it can be seen from simulations that

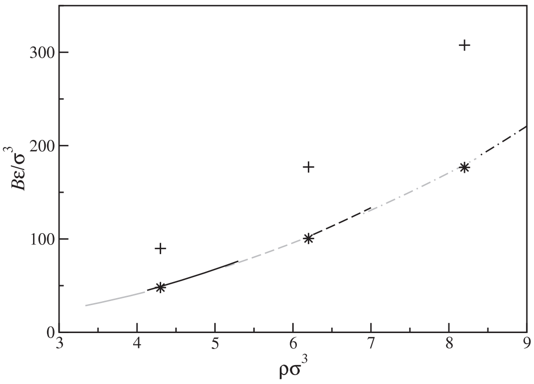

Figure 6. Results for the reduced dimensionless bulk modulus for the GEM-4 system from direct differentiation of the free energy for three different temperatures in the stable crystal structures (fcc (black) and bcc (gray) at $k_{\mathrm{B}}T/\varepsilon = 0.5$ (solid line), $k_{\mathrm{B}}T/\varepsilon = 0.8$ (dashed line) and at $k_{\mathrm{B}}T/\varepsilon = 1.1$ (dotted–dashed line)), along with the values at three state points for B_{vir} (pluses, obtained via (23)) and $B = B_{\mathrm{vir}} - B_{\mathrm{del}}$ (stars).

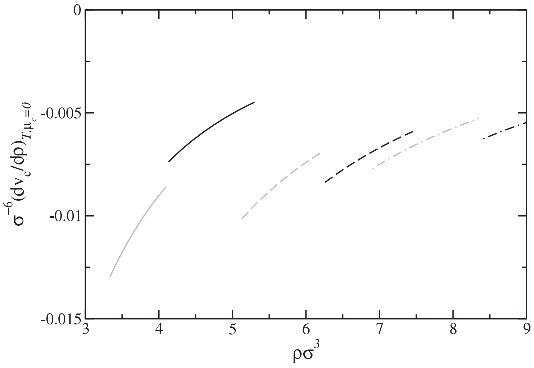

Figure 7. Variation of the primitive cell volume v_{c} with density in equilibrium (i.e. at $\mu_{\mathrm{c}} = 0$) for three different temperatures in the respective stable crystal structures (fcc (black) and bcc (gray) at $k_{\mathrm{B}}T/\varepsilon = 0.5$ (solid line), $k_{\mathrm{B}}T/\varepsilon = 0.8$ (dashed lined) and at $k_{\mathrm{B}}T/\varepsilon = 1.1$ (dotted–dashed line)) of a GEM-4 system.

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[6] Remarkably, although there is incessant hopping of particles from one site to another, rendering these crystals *ergodic* and endowing them with a non-vanishing long-time diffusivity, the underlying crystal structure remains intact. In fact, this does not happen *despite* the hopping mechanism but *because* of it. For details, see [71].

the polydispersity of the clusters decreases as the density increases and particles are less likely to hop between lattice sites. Therefore, the clusters behave more and more like hard spheres. Along with the existence of an almost density-independent lattice constant, this result explains why clustered solids are expected to be stable even at high pressures and/or densities.

5. Conclusions

In this paper, we showed how soft matter particles that repel each other via a special class of soft, bounded interactions can still form clusters which solidify into crystals. To study this behavior with computer simulations, it is essential to adjust the thermodynamic relations to take into account the particular nature of the solid cluster phase. Using this modified formalism, it is then possible to determine the equilibrium cluster occupation number, i.e. the amount of particles per lattice site, within the constraints exerted by typical computer simulations. It has to be stressed that this formalism is also fully relevant in the context of micelle formation. For instance, it was seen that block co-polymers build micelles that can freeze into cubic structures [74]. Also here the equilibrium number of polymer chains per micelle has to be determined via the thermodynamic formalism presented in this paper to guarantee evaluation of equilibrium properties within the simulations. Finally, we note that bounded interactions have recently also become the subject of considerable activity from a mathematical physics perspective, since they allow for the determination of *exact* ground states [75, 76], they admit the application of generalized duality relations [77] and they can be extended to arbitrary dimensions [78].

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