

Cluster-forming systems of ultrasoft repulsive particles: statics and dynamics

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Abstract

In this paper, we present a short review as well as novel results on a recently established counterintuitive phenomenon of cluster aggregation of particles that interact via purely repulsive interactions. We demonstrate how repulsion can lead to clustering provided that the interaction allows full particle overlaps and also displays negative Fourier components. The formation of crystals with average site occupancy that scales linearly with density, and which is in general a noninteger number, is demonstrated by means of density functional theory and Monte Carlo simulations. Noninteger average occupancy of lattice sites is sustained by incessant hopping processes in the crystal, which we observe and quantitatively analyze by means of Molecular Dynamics simulations. The simultaneous presence of relaxative dynamics on the single-particle and arrested dynamics on the collective level leads to an unusual interplay between the two and to novel scenarios of dynamical arrest in the cluster crystal.

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1. Introduction

A recurrent problem in classical statistical mechanics is that of determining the optimal way of arranging N objects confined in a macroscopic volume V in the thermodynamic limit, i.e., $N, V \rightarrow \infty$ with the ratio N/V remaining constant at the value ρ , denoting the average density of the system. Here, the usage of the term *object* instead of the more restrictive one *particle* is intentional. Whereas in atomic systems ‘particle’ means atom or, at most, molecule, in the realm of soft matter physics the constituent entities of the systems of interest are much more complex [1]. Ranging from the relatively simple linear chains, over to star-shaped or branched-shaped polymers and to vesicles and micelles, the mesoscopically-sized building blocks of soft matter are themselves multi-component, deformable aggregates with a huge number of internal degrees of freedom. On the grounds of economy in the description of the problem, it

is behooving to coarse-grain the aforementioned internal degrees and represent the mesoscopic aggregate as a single *object*, a ‘super-particle’ that interacts with its peers via an effective potential. Such effective potentials are also known from the physics of metals, where they arise by tracing out the electronic degrees of freedom [2]. Nevertheless, they are much more flexible in terms of their shapes and tunability: whereas in the former case a handful of fundamental interactions (e.g., Coulomb, Pauli exchange, and spin–orbit coupling) dictate the form of effective interatomic potentials, in soft matter a large variety of factors allows for the realization of an enormous variety of effective potentials [3].

Having sketched the notion of the term *object* in the context of this work, let us now clarify what we mean by *arrangement*. Of central interest here are regular, periodic structures that are formed by the aggregates, leading to so-called *hypermolecular structures*. Which ordered structure is the stable one, given ρ , the absolute temperature T and the effective pair interaction $v(r)$? The answer can be stated simply—it is the one that minimizes the free energy $F = U - TS$, U and S being the

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internal energy and the entropy of the system, respectively. If we are dealing with hard, impenetrable spheres, U vanishes and the problem assumes an equivalence with optimal packing, which maximizes free space and thus entropy: the fcc and hcp-structures follow as the most stable ones [4,5]. If, on the other hand, we are dealing with soft spheres, then at $T = 0$ we have to minimize the energy U : here, a host of unusual crystal structures can be stable [6–11], which serve as candidates for finite temperatures. The stability of such exotic structures has been recently given a geometrical interpretation in the work of Zihlerl and Kamien [12,13]. One can now take the limit of softness to its extremes and consider effective interactions that remain bounded for all r , including $r = 0$. The search for the regular, periodic spatial arrangements that minimize the free energy of N particles that interact by means of such potentials is highly nontrivial because, as will be seen shortly, these defy all intuition and experience gained from hard spheres and closely related systems. Bounded interactions admit no perturbative treatment with some known case as a reference. They are a class of their own and split, as far as crystallization behavior is concerned, into two subcategories: those showing reentrant melting and those showing cluster formation [14].

2. Cluster formation: statics

Exact results in the direction of *proving* that certain crystal structures minimize the (free) energy are rare: the recent work of Sütő [15,16] impresses with its mathematical elegance and power but his proof of the stability of the bcc-structure is restricted to interactions whose Fourier transform $\tilde{v}(k)$ is positive and has finite support, i.e., $\tilde{v}(k) = 0$ for all k exceeding some cutoff value K_c . When we deal with a more general, bounded interaction $v(r) > 0$ that possesses a Fourier transform $\tilde{v}(k)$, some physical intuition has to come into play and quite a few prejudices stemming from diverging interactions must be abandoned. The key property of such interactions, which was first established at the beginning of the millennium [14,17,18], is that, in the fluid phase, they satisfy with very high accuracy the mean-field approximation, i.e.,

$$c(r) = -\beta v(r), \quad (1)$$

where $c(r)$ is the Ornstein–Zernike direct correlation function (dcf) and $\beta = (k_B T)^{-1}$, with Boltzmann’s constant k_B . Eq. (1) above is satisfied with increasing accuracy as density and/or temperature grow. The mean-field character of the fluid has an immediate consequence on the form of the static structure factor, $S(k) = \langle |\hat{\rho}(\mathbf{k})|^2 \rangle$, where $\hat{\rho}(\mathbf{k}) = \sum_j \exp(-i\mathbf{k} \cdot \mathbf{r}_j)$, with \mathbf{r}_j being the position of the j th particle. From Eq. (1) and the Ornstein–Zernike relation [1] the $S(k)$ of the fluid reads as

$$S(k) = \frac{1}{1 + \beta \rho \tilde{v}(k)}. \quad (2)$$

The accuracy of Eq. (2) has been repeatedly confirmed by comparisons with computer simulations for a variety of systems and thermodynamic conditions [14,17]. The celebrated Gaussian core model of Stillinger [19–23], $v(r) = \varepsilon \exp[-(r/\sigma)^2]$ is a

case in point: here, $\tilde{v}(k) = \varepsilon \pi^{3/2} \sigma^3 \exp[-(k\sigma/2)^2]$. Consequently, $S(k)$ assumes at high densities and/or temperatures the shape of a ‘smoothed step function’, showing a depression at $k \lesssim k_\times$ and rapidly reaching the asymptotic value unity thereafter, with the crossover value k_\times given by [17]:

$$\sigma k_\times = 2\sqrt{\ln(\pi^{3/2} \beta \varepsilon \rho \sigma^3)}. \quad (3)$$

The lack of any pronounced structure in $S(k)$, together with the physical meaning of this quantity as a measure of the propensity of the fluid to sustain spontaneous density fluctuations of wavenumber k [24], leads to the conclusion that systems with positive Fourier transforms of the (bounded) $v(r)$ will show reentrant melting at high densities, a property fully confirmed in refined simulations of the Gaussian model [17,25–29]. Reentrant melting also has a dynamical counterpart, manifested in the anomaly in the density-dependence of the long-time self-diffusion coefficient of the Gaussian fluid [30].

The physical situation is completely different if $\tilde{v}(k)$ has negative parts. Let k_* be the value of k for which $\tilde{v}(k)$ attains its most negative value, $-|\tilde{v}(k_*)|$. Eq. (2) then implies that there is a locus of points $(\rho_\lambda, T_\lambda)$ in the (ρ, T) -plane for which $S(k_*)$ diverges. Evidently, this locus is given by

$$k_B T_\lambda = |\tilde{v}(k_*)| \rho_\lambda. \quad (4)$$

Beyond this so-called λ -line, no uniform fluid can be stable, since $S(k)$ would have unphysical negative parts. On the basis of this fact, it has been conjectured that systems with oscillating forms of $\tilde{v}(k)$ will crystallize at all temperatures into solids whose lattice constant will be dictated by k_* alone, independently of the density [14]. And for the lattice constant to be independent of ρ there is only one solution: particles have to form clusters on every lattice site, whose population n_c grows linearly with density. This is a most unusual situation: normally, if one attempts to introduce new particles in a crystal, these would like to populate regions of *low* local density, such as interstitials. Here, the prediction of Ref. [14] states that the opposite will occur: the new particles will migrate to already occupied sites, increasing their occupancy but maintaining the overall crystal structure and its lattice constant at a fixed value: a novel form of cluster formation, at the complete absence of attractions between the cluster-forming entities.

Recently, these predictions have been proven by a combination of density-functional theory (DFT) calculations and Monte Carlo (MC) computer simulations [31,32]. In the DFT-approach, the key property lies in the fact that *all* higher-order dcf’s $c_0^{(n)}$ in the uniform fluid vanish [32]:

$$c_0^{(n)}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n; \rho) = 0, \quad \text{for } n \geq 3, \quad (5)$$

which is a direct consequence of the mean-field approximation [Eq. (1)] for the second-order dcf of these systems [32]. As a consequence of Eq. (5), the excess part of the free energy functional, $F_{\text{ex}}[\rho]$ of arbitrarily inhomogeneous phases takes a simple bilinear form in the density field $\rho(\mathbf{r})$ with the pair interaction as a kernel, viz.:

$$F_{\text{ex}}[\rho] = \frac{1}{2} \iint d^3r d^3r' v(|\mathbf{r} - \mathbf{r}'|) \rho(\mathbf{r}) \rho(\mathbf{r}'). \quad (6)$$

To analyze the stability of cluster crystal phases, the ideal part of the functional [33], $F_{\text{id}}[\rho] = k_{\text{B}}T \int d^3\mathbf{r} \rho(\mathbf{r}) [\ln[\rho(\mathbf{r})\Lambda^3] - 1]$, with Λ the thermal de Broglie wavelength, is added on $F_{\text{ex}}[\rho]$ to build the total free energy functional $F[\rho]$ and the density field is parametrized as a sum of Gaussian orbitals centered on the lattice sites $\{\mathbf{R}\}$, each normalized to the cluster occupancy n_c :

$$\rho(\mathbf{r}) = n_c \left(\frac{\alpha}{\pi} \right)^{3/2} \sum_{\{\mathbf{R}\}} \exp[-\alpha(\mathbf{r} - \mathbf{R})^2]. \quad (7)$$

Contrary to the case of single-occupancy crystals, the functional $F[\rho]$ has to be minimized, in addition to changes of the lattice arrangement and the localization parameter α , also with respect to the site occupancy n_c . Equivalently, the latter minimization can be thought of as a variation of the lattice constant a or the length of the shortest reciprocal lattice vector, K_1 . Indeed, for a given density ρ , K_1 and a scale as $(\rho/n_c)^{1/3}$ and $(\rho/n_c)^{-1/3}$, respectively.

The ideal part of the functional, $F_{\text{id}}[\rho]$, disfavors both spatial modulation of the density and the formation of clusters; indeed, it can be shown [31,32] that there is an ideal entropic penalty associated with cluster formation, which scales as $\sim \ln n_c$. Evidently, it is the excess term that stabilizes crystals and, in particular, cluster crystals. This can be demonstrated in two equivalent ways. The first possibility is to express the density profile in Fourier space and rewrite the excess free energy, Eq. (6), as a sum of contributions from density waves with components only from the reciprocal lattice vectors (RLVs) of the candidate crystal lattice. This approach has been taken in Ref. [32]. Making the additional approximation of taking only the contribution from the first nonvanishing shell of RLVs of the crystal lattice into account, the problem of crystallization can be solved *analytically* and it leads to a host of universal results, which we summarize below.

First, it has been shown that freezing and cluster formation are only possible in the framework of this functional if $v(r)$ has negative Fourier components. In addition, it is established that the magnitude of the first nonvanishing RLV of the crystal *coincides* with the wavenumber k_* for which $\tilde{v}(k)$ takes its (negative) absolute minimum. The stable crystal, immediately after freezing, is bcc and possesses, evidently, a density-independent lattice constant, brought about by the accumulation of more and more particles on the lattice sites as density grows. In fact, for the bcc-crystal the cluster population n_c scales with density ρ as [32]:

$$n_c = \frac{8\sqrt{2}\pi^3}{k_*^3} \rho. \quad (8)$$

This scaling is universal for all bounded potentials $v(r)$ with negative Fourier components, which are termed Q^\pm in Ref. [14]. Additional universal properties are the Lindemann ratio and the Hansen–Verlet value at freezing. The former is determined as $L_f = \sqrt{2}\gamma_f$, where γ_f is obtained as the solution of the implicit equation:

$$\gamma_f^{-1} = -4\pi^2 \left[\ln(\gamma_f\pi) + 1 + \frac{2\ln 2}{3} \right], \quad (9)$$

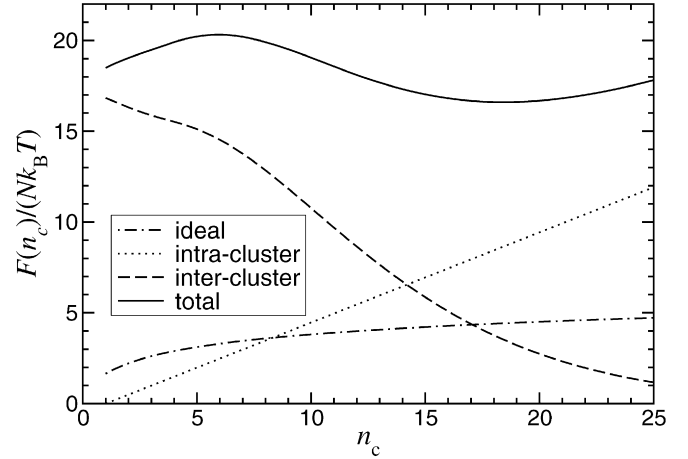


Fig. 1. The ideal, intra- and inter-cluster contributions to the free energy per particle of a fcc cluster crystal formed by GEM-4 particles at temperature $T^* = 1$ and density $\rho^* = 9$. Here, the localization parameter has the value $\alpha\sigma^2 = 45.51$ that minimizes the free energy functional. An optimal value $n_c = 18.4$ for the cluster size is obtained as a result of the competition between the three terms.

yielding $\gamma_f \cong 0.018$ and thus $L_f \cong 0.189$. The latter, $S_f(k_*)$, assumes the universal value

$$S_f(k_*) = \left[1 - \frac{e^{4\pi^2\gamma_f}}{16\pi^2\gamma_f} \right]^{-1} \cong 3.542. \quad (10)$$

The crystallization line (ρ_f, T_f) on the density-temperature plane assumes, according to the approximate theory, the form of a straight line [32]:

$$k_{\text{B}}T_f = 16\pi^2\gamma_f e^{-4\pi^2\gamma_f} |\tilde{v}(k_*)| \rho_f. \quad (11)$$

Contrary to the Lindemann ratio and the Hansen–Verlet value, the freezing locus does depend on the pair potential but it does so in a particularly simple form by scaling linearly with the absolute value $|\tilde{v}(k_*)|$. Moreover, it has been shown that the predictions of the density functional theory are in full agreement with a phonon-based, harmonic theory for the crystal.

An alternative, which also allows to gain insights into the cluster formation, is to express the excess functional in real space, in which case it can be split up into an intra-cluster term, describing the interactions between particles in the same cluster, and an inter-cluster counterpart [31,34]. Whereas the former disfavors cluster formation, the latter works in the opposite direction: indeed, cluster formation implies that the lattice constant grows, thus diminishing the interactions between clusters located at different sites and lowering the free energy of the system.

A particularly simple realization of Q^\pm potentials is offered by the family of the so-called generalized exponential models of exponent n (GEM- n), $v(r) = \varepsilon \exp[-(r/\sigma)^n]$, with $n > 2$ [31,32]. In Fig. 1, we show representative results for the ideal, intra- and inter-cluster contributions to the free energy of the GEM-4 model at reduced temperature $T^* \equiv k_{\text{B}}T/\varepsilon = 1$ and density $\rho^* \equiv \rho\sigma^3 = 9$. It can be seen how the competition between the three terms brings about the global minimum at an optimal value of n_c .

The phase diagram of the GEM-4 model [31] is shown in Fig. 2. It features a first-order transition from a fluid of clus-

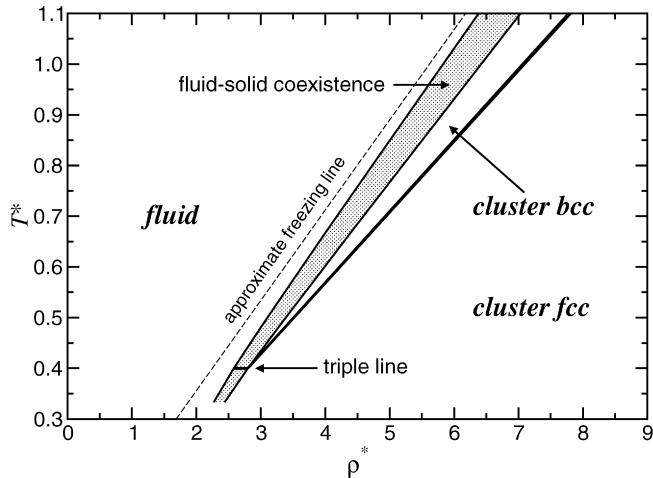


Fig. 2. The phase diagram of the GEM-4 model as obtained by density functional calculations, Refs. [31] and [34]. The dashed line is the approximate freezing locus of Eq. (11).

ters to a cluster bcc-crystal above the triple temperature, and a subsequent structural phase transition from a cluster bcc to a cluster fcc crystal. For both crystals, the first nonvanishing RLV shell lies very close to k_* and is density-independent. Parallel to the DFT-calculations, Monte Carlo simulations have been performed in order to calculate, via Widom insertion, the free energies of the fluid and the crystal [31,34]. Contrary to the case of particles that interact via diverging potentials, Widom's insertion method is highly efficient in this case, since additional particles can be introduced in a cluster crystal with only a small energy penalty, due to the bounded character of the interactions between the constituent particles. The so-determined free energies agree very well with those predicted by DFT, which demonstrates the accuracy of the former.

It must be emphasized that in the simulations of Refs. [31] and [34], the lattice constant of the crystal was *prescribed* to the value predicted by the DFT, determining thereby the size of the cubic simulation box. The fact that the free energies of the crystals from simulation turn out to be in excellent agreement with those predicted by the DFT [31,34], is nontrivial and demonstrates the validity of the latter. Nevertheless, a much more stringent test of both the clustering predictions and the DFT itself is a fully *ab initio* simulation, in which the lattice constant (or, equivalently, the cluster population n_c) are determined without any additional assumptions. In more formal terms, n_c is not a variable that can be externally fixed (such as density or temperature); rather, it is variationally self-adjusted, consistent with the principle of minimization of the free energy with respect to it. The situation bears analogy with the that of the particle number of a photon gas, which indeed cannot be externally constrained to a fixed value, but it is determined by volume and temperature as a self-adjusting variable instead. The task of full determination of n_c without assumptions has been recently accomplished in the simulations of Mladek et al. [35], who developed a novel simulation scheme, apt to deal with the cluster crystals at hand, and which achieves the fulfillment of free adjustment of n_c . These novel results fully confirm all theoretical predictions on the properties of cluster crystals and yield excel-

lent agreement with theory for the melting- and freezing lines of the GEM-4 model.

3. Equilibrium dynamics of cluster crystals

Whereas in atomic crystals multiple site occupancies are prohibited and vacancies usually have extremely small concentration, and can thus be ignored as a first approximation [36], the cluster crystals at hand are completely different because, in a sense, they are full of defects. By *defects* we mean here that, since the optimal value of n_c is in general a real noninteger number, the lattice site occupancy at any given moment in time is disordered: the instantaneous (integer) populations of the sites have considerable polydispersity. A perfect crystal is, of course, mechanically unstable if sites have permanently different occupancies. Mechanical stability must be maintained on average, by means of dynamical events that guarantee the equality of the time-average site occupancy n_c for all sites. In the cluster crystals, there must exist incessant hopping processes that allow for the exchange of particles between sites. Whether hopping merely amounts to *local* particles moves or it takes the form of diffusive migration of particles across macroscopically large distances, remains to be seen. Either way, a mechanism which restores a *single* average occupancy for all lattice positions is necessary. The equilibrium dynamics within the cluster crystals seems therefore to be quite different from that known for perfect atomic crystals, for which particle motions are restricted to lattice oscillations (phonons).

In order to shed light into the cluster crystal dynamics, Moreno and Likos have recently performed extensive Molecular Dynamics (MD) simulations for the GEM-8 model [37], which has a shorter interaction range than the GEM-4. This choice reduces the computational expense for investigation of slow dynamics (note that the simulated densities in GEM-models are much higher than the values $\rho^* \sim 1$ typically used for, e.g., Lennard–Jones systems). Evidence of hopping processes of the particles between lattice sites has been found, both in the calculation of the single-particle van Hove function and in that of the mean squared displacement $\langle \Delta r^2(t) \rangle$. In fact, the latter shows three regimes: for short times, an oscillatory motion around the lattice site has been detected, whose period scales as $\rho^{-1/2}$ and is temperature-independent, in agreement with theoretical predictions [32]. For intermediate time scales, a plateau is reached and for longer times, typical diffusive behavior is seen, with $\langle \Delta r^2(t) \rangle$ scaling linearly with time t . Diffusion is caused by particle hopping, preferentially from each site to one of the nearest neighbors, as inferred from the succession of local maxima and minima exhibited by the single-particle van Hove function [37].

Fig. 3 shows a map of the local potential energy that a test particle feels in a fcc-crystal of GEM-8 particles for one representative snapshot along the simulation run. The deepest regions of the energy are centered around the lattice sites; these are separated by barriers whose height is minimum across nearest-neighbor distances. In agreement with the property $n_c \propto \rho$, the height of these barriers scales with density, $\Delta U/\varepsilon =$

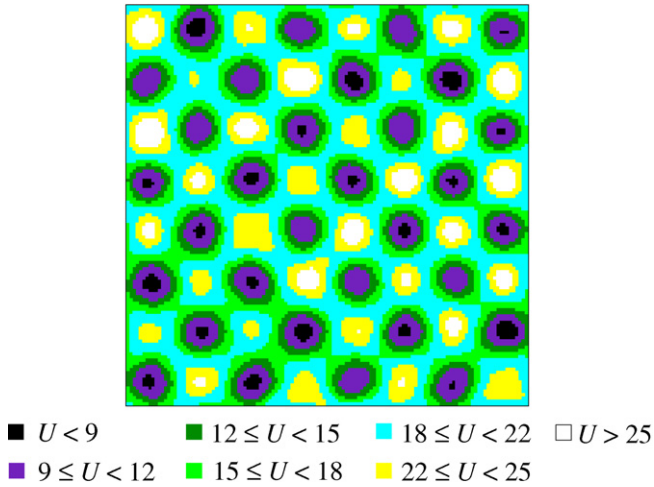


Fig. 3. Projection of the potential energy U of a GEM-8 model (measured in units of ε) on a [001] lattice plane, for a configuration of the fcc-crystal at $\rho^* = 5.0$ and $T^* = 0.667$. Darker colors represent lower energies (see legend) and are centered around lattice sites.

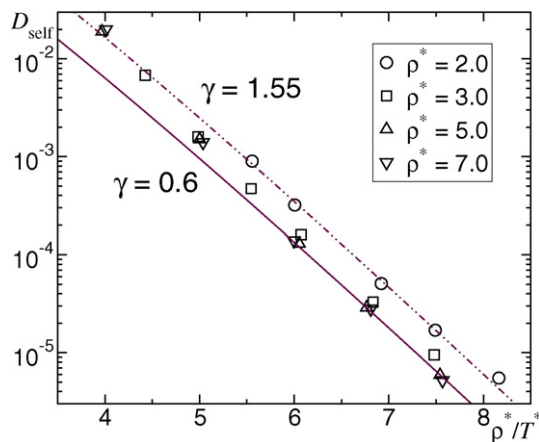


Fig. 4. The long-time self-diffusion coefficient D_{self} in GEM-8 fcc-crystals as measured by simulation (points) for different values of density and temperature. The broken and solid lines are fits to the data according to Eq. (12) with the corresponding values of γ shown in the plots. Here, the potential barrier $\nu = 2.3$, determined from the distribution of local potential energies of the crystalline solid, is not a fit parameter.

$\nu\rho^*$ with the proportionality constant ν being model-dependent and having the value $\nu \cong 2.3$ for the GEM-8 system.

The physics of the diffusion can be understood by modeling each site with a harmonic well of height ΔU and each particle with a thermal oscillator at temperature T . Calculating the probability that the oscillator's total energy E exceeds ΔU is straightforward and can be immediately translated into a hopping probability $P_{\text{hop}}(\Delta U)$. The long-time self-diffusion coefficient D_{self} then follows by the standard theory of random walks and it takes the form

$$D_{\text{self}} = \gamma(x^2 + 2x + 2)e^{-x}, \quad (12)$$

where $x \equiv \nu\rho^*/T^*$ and γ is some coefficient of order unity. Comparisons with simulation results fully support this interpretation, see Fig. 4. For cluster crystals formed by Q^\pm -particles,

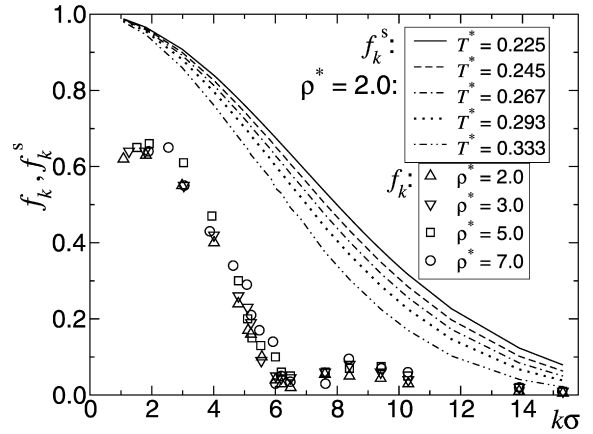


Fig. 5. The k -dependence of the nonergodicity parameters for self- (f_k^s , lines) and collective (f_k , symbols) dynamical density correlators. Data for f_k^s are displayed for fixed $\rho^* = 2.0$ and several temperatures. Data for f_k are shown for different densities and correspond to state points above the localization transition. Data for f_k are only shown for k -values not belonging to the reciprocal lattice.

the long-time self diffusion is dictated by the ratio of density to temperature—a dynamical extension of static properties of the system [32].

The self- and collective dynamical density correlators $F_s(k, t)$ and $F(k, t)$ have also been measured in the MD simulations of Ref. [37]. For values of k probing the lattice structure (i.e., reciprocal lattice vectors), $F(k, t)$ does not show a long-time decay, which is consistent with the stability of the lattice structure. For other values of k , a dynamical decoupling of self- and collective correlations is observed, if one considers the behavior of the plateau height (nonergodicity parameter) of the two correlators at intermediate times. Whereas the plateau value f_k^s of $F_s(k, t)$ grows as T is lowered, for the same range of temperatures, the height f_k of $F(k, t)$ remains constant. This feature suggests that the localization transition for out-of-lattice collective correlations occurs at lower temperature than for single-particle motions, in analogy with the behavior of plastic crystals [37]. However, in the present system the aforementioned hopping processes act to restore ergodicity for self-dynamics, moving the particles beyond the localization length. As a consequence, also the self-correlators decay from the plateau to zero at sufficiently long times.

Results for f_k (excluding k -values that coincide with RLVs) above its localization transition (i.e., T -independent) are shown in Fig. 5 for the investigated densities. The approximate scaling behavior of f_k agrees with a common lattice constant for all the densities. Since $n_c \propto \rho$, the major effect of increasing n_c on $F(k, t)$ is a rescaling of ρ_k , which is canceled after normalization of $F(k, t)$. The T -dependence of f_k^s is also shown at a fixed density $\rho^* = 2.0$. The localization length for the self-correlators (which is proportional to the inverse width of f_k^s) grows with temperature, consistent with the larger amplitude of site oscillations as the temperature is increased. The smaller width of f_k as compared to f_k^s indicates a much weaker localization for collective than for self-motions.

4. Conclusions

Ultrasoft repulsive particles of the Q^\pm class form a novel type of interactions with unusual and counterintuitive properties centered around the formation of ordered cluster arrangements. Though apparently academic at first sight, the systems described in this work can be realized experimentally: amphiphilic dendrimers that have been modeled in computer simulations have precisely the type of Q^\pm -interactions that have been employed in this work [38]. Moreover, it must be emphasized that the presence of a short-range hard core will barely affect the phenomena discussed in this work, as long as its range is considerably shorter than that of the soft shoulder. This has been convincingly demonstrated in the recent work of Glaser et al. [39], who extended the clustering criterion of Ref. [14] to potentials with a hard core and found cluster formation for such model systems as well. Future directions should focus on the one hand towards the search of experimental realizations of the clustering phenomena and on the other on studies of the properties of these systems under confinement, as well as on the nucleation dynamics of the cluster crystals.

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