Reentrant and Isostructural Transitions in a Cluster-Crystal Former

Kai Zhang,[1] Patrick Charbonneau,[1,*] and Bianca M. Mladek[2,†]

[1]*Department of Chemistry, Duke University, Durham, North Carolina, 27708, USA*

[2]*Department of Chemistry, University of Cambridge, Lensfield Road, CB2 1EW, UK*

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Abstract

We study the low-temperature behavior of a simple cluster-crystal forming system through simulation. The phase behavior is found to be hybrid between the Gaussian core and penetrable sphere models. The system additionally exhibits a series of reentrant crystallization and melting loops as well as critical isostructural transitions between crystals of different occupancy. Due to the creation and annihilation of lattice sites, the system further shows an unusual and intriguing softening upon compression.

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*Electronic address: patrick.charbonneau@duke.edu

†Electronic address: bmm32@cam.ac.uk

Since van der Waals and Kirkwood, we better appreciate the fundamental role of harshly repulsive interactions in the organization of matter [1]. But what happens when harshness turns to softness? Core softened potentials can exhibit microphase separation [2], reentrant melting, and isostructural phase transitions [3] in systems as diverse as Cerium metal [4], star polymers [5], dipolar spheres [6], electron bubbles [7, 8], and rotating Bose gases [9]. Even softer, *coreless* repulsive interactions are also found in complex systems. Nonlinear fields can form particle-like structures governed by solitonlike interactions [10, 11]; and the centers of mass of structures with low fractal dimension, such as polymers [12], dendrimers [13, 14], and microgels [15], can be immaterial and thus overlap with only a finite free energy penalty. As a result, materials governed by such interactions can exhibit quite an unusual phenomenology compared to "simple" matter [16]. Soft core models are further used to study the difficult glass [17, 18] and classical ground state determination problems [19, 20], highlighting the broad interest in the phase behavior of systems with soft potentials.

A certain universality permeates the thermodynamic assembly of bounded, purely repulsive interactions. Two phenomenological categories have been identified. Systems with pair interactions whose Fourier components are purely positive show reentrant melting, while those with some negative Fourier components cluster and freeze into multiply occupied crystals (MOC) [17, 21–27]. A continuous crossover between the two categories can be realized via the tuneable generalized exponential model of index n (GEM-n) [23], whose pair potential for particles a distance r apart is

$$\phi(r) = \varepsilon \exp\left[-(r/\sigma)^n\right], \tag{1}$$

with ε and σ setting the units of energy and length, respectively [28]. Upon compression at low temperatures, the $n = 2$ Gaussian core model (GCM) [29] forms cubic crystals that eventually remelt [30, 31]; and all GEM-n of $n > 2$ are predicted to show MOC clustering [22], including the $n \to \infty$ limit, i.e., the penetrable sphere model (PSM) [21].

For strong interactions (or effective low temperatures), which may be the most experimentally accessible and where coarse-grained pairwise interactions for complex systems are most reasonable, the phase behavior of MOC-forming systems is not understood. Various plausible ordering scenarios are suggested by theory and experiments: DFT predicts a continuous increase in clustering [22, 23]; the PSM limit presents a sequence of second-order phase transitions between crystals of increasing occupancy [21]; and bubble solids alternate

liquid and crystal phases of increasing lattice occupancy [7]. A cascade of pure first-order isostructural solid-solid transitions between crystals of different occupancy is also plausible, as theoretically predicted by [32]. Such isostructural transitions should terminate at critical points, because the cluster occupancy of high-temperature MOC-formers increases continuously with density [23, 24]. A rare example of this type of critical point is found in pure Cerium, where a pressure-induced electronic promotion underlies the transition between two isostructural solids with different lattice spacing. Cerium's properties are, however, difficult to study [4, 33]. Critical points involving volume collapse have also been predicted for a variety of purely classical, effective interaction potentials [3, 34]. But the experimental colloidal systems in which they could be observed have an intrinsic size polydispersity [35] or an effective interaction [16] that prevents phase separation. The relatively broad lattice spacing of MOC suggests that crystal formation should be less sensitive to these experimental constraints. In this manuscript, we present a computational study of the low-temperature behavior of the MOC-forming GEM-4, whose behavior is shown to be a complex hybrid between the GCM and the PSM limits, and in which we find reentrant transitions and evidence for a cascade of isostructural transitions.

We perform lattice Monte Carlo simulations [37] of the GEM-4 model, whose high-temperature behavior was previously determined [24], for $N = 1000$-5000 particles at constant N, volume V, and temperature T. The pressure P is obtained from the virial and the Helmholtz free energy F of the different phases is calculated via thermodynamic integration. The reference system is the ideal gas [36], and for the body-centered cubic (bcc) and face-centered cubic (fcc) crystal phases, potential wells centered around the N_c lattice sites of the corresponding crystal symmetry are included [27]. This crystal reference, which allows for the characteristic multiple occupation of lattice sites and for particle hopping between those sites, permits a reversible integration path. For a fixed number density ρ, the lattice site occupancy $n_c = N/N_c$ at equilibrium is identified for every state point by simulating a crystal phase at various fixed n_c then minimizing the resulting constrained free energy $F(n_c)$, i.e., identifying the loci (Fig. 1)

$$F(n_c^{\rm eq}) = \left[\frac{\partial F(n_c)}{\partial n_c}\right]_{\rho,T} = 0, \tag{2}$$

similarly to what was done for identifying the equilibrium phase in a modulation-forming spin system [38]. This scheme is also related to that used for GEM-4's high-T phase dia-

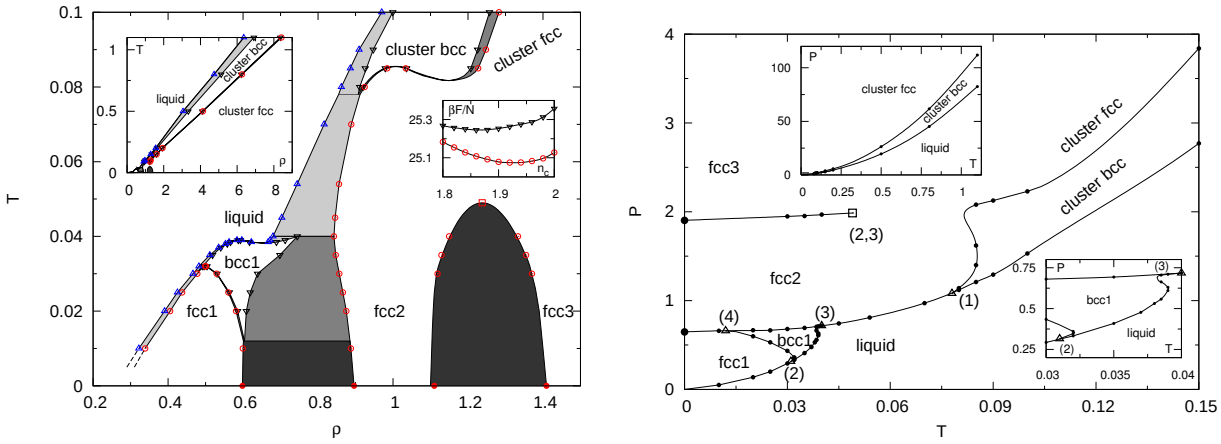

FIG. 1: (Color online) T-ρ (left) and $P-T$ (right) low- and high-T (left insets [24]) simulation phase diagrams. The isostructural critical point (□) is extrapolated from the law of rectilinear diameters [36] and the $T=0$ results (●) come from phonon theory [32]. Left: The coexistence regions (shaded) are delimited by simulation results for liquid (△), bcc (▽), and fcc (⊙) phases. The free energy per particle for the bcc (▽) and fcc (⊙) phases at $T=0.03$ and $\rho=0.85$ shows that a fcc with $n_c^{\rm eq}=1.94(1)$ is the ground state (right inset). Right: The phase boundaries (solid lines) are guides for the eye that are consistent with the Gibbs-Duhem slopes (not shown) at the coexistence points (·). The triple points (△) are numbered. The right inset enlarges the liquid reentrance region.

gram determination, where n_c was iterated until the (unphysical) field conjugate to n_c had vanished [24, 39]. The earlier approach allows for a gradient-based minimization of the free energy, but relies on an additional independent calculation of the chemical potential at fixed n_c. It breaks down at low T, where its numerical determination cannot be efficiently resolved by Widom's particle insertion [36].

The low-T phase diagram shown in Fig. 1 is determined through common tangent construction of the free energy data. A linear transformation with parameter κ of the free energy $\beta\tilde{F}\rho/N=\beta F\rho/N-\kappa\rho$, where β is the inverse temperature, enhances the visibility of the coexistence regime (Fig. 2). As anticipated from the high-T extrapolation, the cluster bcc phase vanishes at a triple point $T_{\rm t}^{(1)}=0.078(1)$, but surprisingly the transition is preceded by a reentrance crystallization loop. Because the tail of the GEM-4 decays faster than any inverse power, the liquid freezes into a single-occupancy fcc (fcc1) that reaches vanishingly small densities at low T, in agreement with predictions from genetic algorithms [40, 41] and

phonon theory [32].

Upon increasing the density below $T_t^{(1)}$ the phase diagram exhibits a rich and interesting behavior. GCM-like phase behavior [29–31] is followed by a clustering regime. First, the fcc1 phase gives way to a single-occupancy bcc (bcc1) phase at a second triple point $T_t^{(2)} = 0.031(1)$. For a narrow temperature range above $T_t^{(2)}$, a bcc1 wedge between the liquid and the fcc1 phase leads to reentrant freezing of bcc1 upon compression. At $T = 0.039(1)$ a maximum freezing temperature for bcc1 is observed, which leads to reentrant melting upon compression and a sigmoidal coexistence line on the P-T phase diagram, as observed in the soft core model [3, 4]. Here the reentrant liquid range spreads only over a finite density regime $0.59 \lesssim \rho \lesssim 0.68$ and over a much smaller temperature range $0.0385 \lesssim T \lesssim 0.039$ than in the canonical GCM [29–31]. The intermediate nature of the GEM-4 suggests that this behavior might become more pronounced as the GCM is approached, i.e., $n \to 2^+$, and should disappear before the PSM limit $n \to \infty$, where reentrance is not expected. The connection to the high-temperature regime occurs through a third triple point $T_t^{(3)} = 0.040(1)$. A prior, coarser study of the liquid-crystal transition in this regime missed both presence of fcc1 and of the reentrant melting [42]. It also assigned the unusual shape of the liquid-crystal coexistence curve to the onset of clustering, which is not quite accurate. It is rather the presence of reentrant melting that changes the coexistence behavior.

Clustering does lead to a qualitatively different phase diagram topology, but at densities well away from the liquid phase. At low T the nature of clustering is unlike what is seen at higher T, where n_c changes linearly with ρ resulting in a lattice constant that is nearly density independent [24]. Here, the lattice occupancy is quasi-quantized, and at very low T the lattice constant changes discontinuously through isostructural transitions between fcc lattices of nearly perfect integer occupancy $n_c \leftrightarrow n_c+1$ (Fig. 2). The first occurrence of these transitions, fcc1 $\leftrightarrow$ fcc2, is partially obscured by the bcc1 phase, down to the fourth triple point $T_t^{(4)} = 0.012(1)$ (Fig. 1). At higher densities, the fcc2 $\leftrightarrow$ fcc3 coexistence is fully developed and no other liquid or crystal phases are found to interfere. Genetic algorithm results further suggest that no other crystal symmetry should be stable at higher densities [40, 41]. It is at the moment computationally difficult to go beyond fcc3, but both a zero temperature treatment paired with phonon theory [32] and a simple mean-field cell theory predict a cascade of isostructural transitions to carry on *ad infinitum*, slightly broadening the finite T coexistence regime between two integer occupancies. As previously argued the topology of

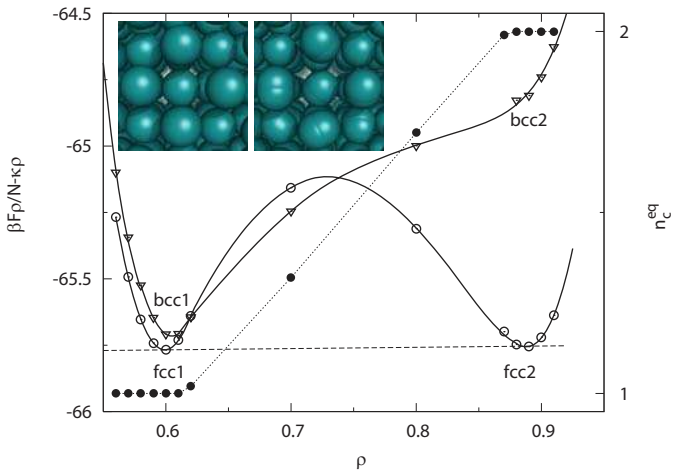

FIG. 2: Free energy curves of the stable fcc ($\odot$) and, for comparison, the metastable bcc ($\triangledown$) structures at $T = 0.01$ with $\kappa = 142.7$. Both curves show the van der Waals loop characteristic of a system whose limited size inhibits phase separation. The coexistence densities of the fcc1 (left inset)-fcc2 (right inset) isostructrual transition are determined by the common tangent construction (dashed line). The equilibrium lattice occupancy $n_c^{\rm eq}$ ($\bullet$) plateaus near integer values for the thermodynamically stable phases.

the phase diagram demands that each isotructural transition terminate at a critical point, the first one of which is $T_c^{(2,3)} = 0.049(3)$. The critical exponents are expected to be of mean-field character [22, 43]. Hopping between lattice sites should eventually depress the critical temperature with increasing n_c. The series of first-order isostructural transitions contrasts with the continuous second-order clustering transitions for the PSM predicted by cell theory [21]. This last result suggests that the behavior of the PSM might be singular, but further studies are necessary to clarify the nature of the phase behavior of the GEM-n family as $n \to \infty$.

One of the key material properties of MOC is the presence of two distinct microscopic mechanisms for responding to compression. Like any other crystal, MOC can affinely reduce their lattice constant, but additionally they can eliminate lattice sites by increasing the mean lattice occupancy. We can decompose the bulk modulus

$$B \equiv V \left(\frac{\partial^2 F}{\partial V^2} \right)_{N,T} = B_{\rm vir} - B_{\rm corr} \tag{3}$$

into a virial contribution at constant lattice occupancy $B_{\rm vir}$ and a "softening" correction $B_{\rm corr}$ that map directly onto the two microscopic mechanisms [24, 45]. At high T, the

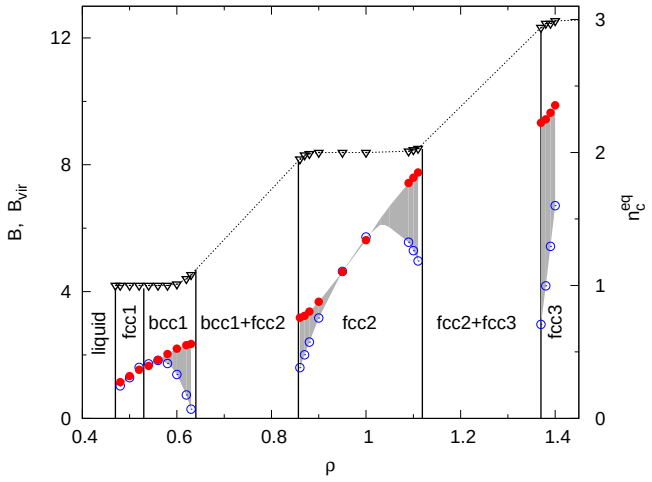

FIG. 3: (Color online) Isothermal ($T = 0.03$) bulk modulus B ($\odot$), its virial contribution ($\bullet$) and softening correction (shaded), and $n_c^{\rm eq}$ ($\triangledown$) [44]. The solid vertical lines indicate phase boundaries.

additional softening contribution can be as high as half the virial component [24]. In low T crystals, the quasi-quantized jumps in lattice occupation lead to quite a different behavior. Away from the coexistence regions, where the lattice occupancy is nearly constant, the system responds only affinely to isothermal compression. The virial contribution to the bulk modulus captures the full response of the system, that is, $B_{\rm corr} \sim 0$, as observed in Fig. 3 [44]. The quantization is, however, not perfect, which leads to interesting mechanical properties in the softening regions that precede and follow the phase transitions, where the lattice occupancy deviates slightly from integer values. Near the bcc1-fcc2 transition, for instance, $B_{\rm corr}$ is nearly equal to the virial contribution, which means the system exerts no resistance to compression. This very rapid change in mechanical properties with compression is uncommon, and may lead to interesting novel material behavior. The different physical nature of the virial and softening contributions suggest that there might be a separation of time scales for the microscopic relaxation. Hardening or softening of the material upon compression might thus depend on the deformation rate.

We have presented the intriguing low-temperature phase behavior of the MOC-forming GEM-4 through a computational method specially designed for this class of systems. The complexity of the phase behavior is particularly noteworthy considering the simplicity of the model, which is free of competing length scales. Experimental soft matter realizations of cluster crystals are still lacking, but large-scale, monomer-resolved simulations of am-

phiphilic dendrimers that show clustering are currently under way [46]. Importantly, the approach outlined in the present work should be directly applicable to phenomena of reversible clustering in other branches of physics. Examples are: the structures formed by the soft solitons of Refs. [10, 11], the quasi-2d electron bubbles in the quantum-Hall regime [7, 8] and the predicted clustering of vortex lines in rotating Bose gases [9].

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