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Soft spheres make more mesophases

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Abstract – We use both mean-field methods and numerical simulation to study the phase diagram of classical particles interacting with a hard core and repulsive, soft shoulder. Despite the purely repulsive and isotropic interaction, this system displays a remarkable array of aggregate phases arising from the competition between the hard-core and soft-shoulder length scales, including fluid and crystalline phases with micellar, lamellar, and inverse micellar morphology. In the limit of large shoulder width to core size, we argue that this phase diagram has a number of universal features, and classify the set of repulsive shoulders that lead to aggregation at high density. Surprisingly, the phase sequence and aggregate size adjust so as to keep almost constant inter-aggregate separation.

Entropy is a potent force in self-assembly. It can be argued, through entropic considerations alone, that hard spheres will self-assemble into the face-centered-cubic (fcc) lattice or any of its many variants related through stacking faults. As a result, when a material exhibits an fcc phase, it is often attributed to the optimality of the close-packed lattice. On the other hand, the stability of the less common or less dense lattices is interpreted in terms of a range of explanations including basic quantum-mechanical arguments [1], lattice effects [2], partially filled Landau levels [3,4], and soft interactions [5–7]. While there has been concerted effort to tailor the pair interaction to achieve a desired periodic arrangement [8] this must be done in the context of those packing motifs that arise from generic interactions. For instance, it would be fairly trivial to design a potential to make an fcc lattice.

With this in mind, here we consider a seemingly simple extension of the hard sphere model, namely a hard-core/soft-shoulder (HCSS) interaction:

$$V_{\mathrm{HCSS}}(r) = \begin{cases} \infty & r < \sigma \\ \epsilon & \sigma < r < \sigma_s \\ 0 & r > \sigma_s \end{cases}, \qquad (1)$$

where σ and σ_s are the core and shoulder radii, respectively, and ϵ is the shoulder height. Such a model with $\sigma_s/\sigma \gtrsim 1$ has been used to study isostructural transitions in Cs and Ce [9]. In HCSS and related potentials, it has been shown that as the range of the soft repulsion grows (corresponding to $\sigma_s/\sigma \approx 2$) a rich variety of density-modulated ground states appear [10–13] which can be characterized as periodic arrangements of regular sized aggregates of the original spheres. In this letter we establish a sufficient condition on the pair potential for aggregation and the subsequent ordering of the aggregates which generalizes results on soft potentials without hard cores [14]. We develop a self-consistent field theory for soft repulsion and use it to study the formation of lamellar phases. We corroborate our analytic treatment with numerical solutions that also predict the existence of hexagonal and inverse hexagonal aggregate phases with both fluid and crystalline intra-aggregate order (fig. 1). In addition, we present results from Monte Carlo simulations of the HCSS potential which both stimulate and support the more general theoretical predictions. In all cases, we find that over the range of stable aggregate structures the lattice constant remains fixed while the aggregates change their size and morphology so as to maintain the average intra-aggregate density ρ.

Why should repulsive potentials lead to aggregation? We can understand this in the context of the HCSS

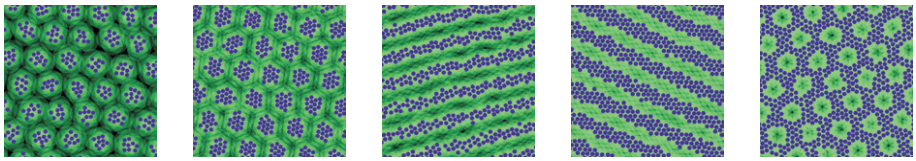

Fig. 1: (Color online) Snapshots from Monte Carlo simulations of the solid and liquid modulated phases of two-dimensional hard-core/soft-shoulder particles with $\sigma_s/\sigma = 5$; shown are the solid (M_s) and liquid (M_l) micelle phases, solid (L_s) and liquid (L_l) lamellar phases, and the solid inverse micelle phase (IM_s). The blue circles are the hard cores of the particles and the overlapping diffuse green circles represent their soft shoulders.

model: consider a uniform density of spheres at densities just large enough so that the soft-shoulders only begin to touch the hard cores. The energy can be lowered by, for instance, bringing pairs of spheres together —moving two spheres closer requires no additional energy, but by reducing the number of nearest neighbors the overall energy is reduced. Indeed, the same physics drives the formation of a multiply-occupied clusters of penetrable spheres ($\sigma = 0$) [15], while the ground state of a generalized exponential repulsion [16] is a multiply-occupied fcc lattice with a lattice constant independent of the average density.

To explore the HCSS ensemble we introduce a lattice model with occupation $n_i = 0, 1$ at each site to enforce the hard-core repulsion. The remaining soft shoulder is characterized by an interaction $V_{\rm SS}^{ij}$ and the density is set through the chemical potential μ in the Hamiltonian:

$$\mathcal{H}[n_i] = \frac{1}{2}\sum_{ij} n_i V_{\rm SS}^{ij} n_j - \sum_i \mu n_i \ . \tag{2}$$

Note that the sum is not over nearest neighbors but over all sites —the range of the interaction is encoded in $V_{\rm SS}^{ij}$. This model with a square-shouder $V_{\rm SS}$ was used to study electron liquids in weak magnetic fields [3,4]. There it was a toy model of the true interactions, while here we study its consequences for generic $V_{\rm SS}$. To develop a mean-field theory, we rewrite the partition function in terms of a continuous field ϕ through the Hubbard-Stratonovich transformation[1]

$$\mathcal{Z} = \sum_{n_j}\int [{\rm d}\phi]\exp\Bigg\{-\frac{\rho_0^2}{2\beta}\int\frac{{\rm d}^d k}{(2\pi)^d}\phi(\mathbf{k})V_{\rm SS}^{-1}(\mathbf{k})\phi(-\mathbf{k}) + \sum_j n_j(i\phi_j + \beta\mu)\Bigg\}, \tag{3}$$

where we have used both continuum and discrete variables to simplify the notation; d is the dimension of space[2]. Here $\rho_0 = \gamma_d \sigma^{-d}$ is the density of the lattice where we have chosen the lattice constant to equal the hard sphere diameter σ and γ_d is a lattice and dimensionally dependent geometrical factor. Summing over $n_j = 0, 1$ results in the exact partition function

$$\mathcal{Z} = \int [{\rm d}\phi]\exp\Bigg\{-\frac{\rho_0^2}{2\beta}\int\frac{{\rm d}^d k}{(2\pi)^d}\phi(\mathbf{k})V_{\rm SS}^{-1}(\mathbf{k})\phi(-\mathbf{k}) + \sum_j \ln\left[1+\exp\left(\beta\mu + i\phi_j\right)\right]\Bigg\}. \tag{4}$$

The average site occupation is $\langle n_i\rangle = \beta^{-1}{\rm d}\ln\mathcal{Z}/{\rm d}\mu = \lambda e^{i\phi_i}/(1+\lambda e^{i\phi_i})$, where $\lambda = e^{\beta\mu}$ is the fugacity. This is related to the number density profile through $\rho_i = \rho_0\langle n_i\rangle$. Note that the presence of the hard cores introduces a new length scale σ which competes with the overlap of the shoulders at σ_s. Equation (4) can be used as the basis for a systematic expansion about the mean-field solution, governed by the equations $V_{\rm SS}^{-1}(\mathbf{k})\phi(\mathbf{k}) = i\beta\rho(\mathbf{k})/\rho_0^2$. Nevertheless, we will consider only the mean-field theory in what follows.

We first consider the stability of fluctuations around a uniform density, following refs. [14,17,18]. In the mean-field approximation, we can recast eq. (4) in terms of the free energy for fixed ρ (*not* fixed μ), obtained via the Legendre transform, to recover the standard density functional form:

$$\beta F = \frac{\beta}{2\rho_0^2}\int\frac{{\rm d}^d k}{(2\pi)^d}\rho(\mathbf{k})V_{\rm SS}(\mathbf{k})\rho(-\mathbf{k}) + \int {\rm d}^d r\left[\rho\ln\left(\rho/\rho_0\right) + \left(\rho_0-\rho\right)\ln\left(1-\rho/\rho_0\right)\right]. \tag{5}$$

Working to quadratic order in fluctuations about a constant ρ we find an instability when both $V_{\rm SS}^{-1}(\mathbf{k}) < 0$ and $\rho_0 \leqslant \rho/\rho_0\left(1-\rho/\rho_0\right)\beta|V_{\rm SS}(\mathbf{k})|$. This stability criterion is a generalization of the result in ref. [14] which we recover at low volume fractions, when $\rho/\rho_0 \to 0$ and the hard cores rarely overlap.

To simplify our analysis of the mean-field lattice model, we first consider the stripe phase. We need only consider Fourier modes which belong to the reciprocal lattice of the periodic structure (including the $\mathbf{k} = 0$ mode). Fixing the zero mode of the density, we find that the wave vectors

[1] Because it oscillates in sign, $V_{\rm SS}(\mathbf{k})$ has a zero and is not invertible. We can, however, decompose $V_{\rm SS} = V_+ - V_-$ into nonvanishing potentials and introduce *two* dummy fields $\phi_\pm$ to complete the Hubbard-Stratonovich transformation. This does not alter the mean-field equations. See Park Y. and Fisher M. E., *Phys. Rev. E*, **60** (1999) 6323.

[2] Our Fourier transform convention has $\phi(\mathbf{k})$ with units of volume, $V_{\rm tot}$, and $V_{SS}(\mathbf{k})$ has units $V_{\rm tot}^{-1}$.

$\mathbf{k}$, where $V_{\rm SS}(\mathbf{k}) < 0$ are unstable, and that the strongest instability will be at the *most negative* value of $V_{\rm SS}$. In case of the soft shoulder in two dimensions, $V_{\rm SS}(\mathbf{k}) = \epsilon\sigma_s J_1(k\sigma_s)/k$, which has a minimum at $k^*\sigma_s \approx 2\pi/1.22$. In other words, the lattice spacing $L = 2\pi/k^* = 1.22\sigma_s$, in very good agreement with both Monte Carlo simulations and off-lattice theory as shown below.

To better understand how the presence of the hard core competes with the soft shoulder in determining the aggregate morphology, we analyze the mean-field behavior of eq. (4) far below the instability to clustering. At low temperatures, we expect cluster occupancy to saturate (*i.e.* $\langle n_i \rangle = 1$ inside the clusters), and we further expect the boundaries between occupied and unoccupied sites to be narrow. In this limit, we use a Sommerfeld-like expansion to compute $\rho(\mathbf{r})$ for a lamellar configuration to lowest order in Δ, the width of aggregate boundary. As is the case for the square shoulder, we assume that $|V_{\rm SS}(\mathbf{k})|$ decays sufficiently rapidly with $|\mathbf{k}|$ and that the *potential*, $\phi(\mathbf{r})$, is well approximated by $\phi(\mathbf{r}) \simeq \phi_0 + \phi^* \cos(k^* x)$. These coefficients are related by the mean-field equation to appropriate Fourier modes of the density. At sufficiently low temperature the density is a step function, and the relevant Fourier modes are $\rho(k=0)/V_{\rm tot} = \rho_0 k^* \ell/2\pi$ and $\rho(k^*)/V_{\rm tot} = \rho_0 \sin(k^*\ell/2)/\pi$, where $V_{\rm tot}$ is the total volume (note that ϕ_0 and ϕ^* are *not* Fourier modes) and ℓ is the width of the lamellae. Simultaneously, the nonlinear relation between ρ and ϕ gives an additional constraint on the position of the interface, $x = \ell/2$, since $\rho(\ell/2) = 1/2$. This leads to $-\beta\mu = i\phi_0 + i\phi^* \cos(k^*\ell/2)$. Combining this with the mean-field equations, we eliminate ϕ_0 and ϕ^* to find a transcendental equation for ℓ:

$$\frac{V^*}{\pi} \sin k^*\ell = V_0 \frac{k^*\ell}{2\pi} - \mu, \tag{6}$$

where $V_0 \equiv V_{\rm SS}(0)/\rho_0$ and $V^* \equiv |V_{\rm SS}(k^*)|/\rho_0$. When we have a soft shoulder, $V_0 \gg V^*$ and $k^*\ell/2\pi \simeq \mu/V_0$. Temperature does not strongly affect the width of the aggregates, but it does alter the sharpness of inner domain boundary. The width of the interface is measured from the slope of the density at the interface, and is given by $\Delta^{-1} = |\rho^{-1}(\mathrm{d}\rho/\mathrm{d}x)|$ at $x = \ell/2$. To lowest order, we find $k^*\Delta/2\pi \simeq k_B T/[2V^* \sin^2(\pi\rho/\rho_0)]$. Therefore, we can see that the aggregates "melt" from the boundaries as the temperature is raised due to the fact that the depth of the self-consistent potential is proportional to V^*. We deduce a rough estimate of the melting temperature of the lamellae, T_m, from the condition that $k^*\Delta/2\pi \lesssim 1$ for ordered structures, or $k_B T_m \sim V^* \sin^2(\pi\rho/\rho_0)$. From this we see that the most stable structures occur at *half-filling*, when $\rho_0 = 2\rho$, consistent with our instability criteria. These calculations can be repeated for the other morphologies by utilizing more modes, $\mathbf{k}_i$ with $|\mathbf{k}_i| = k^*$ and $\sum_i \mathbf{k}_i = 0$.

Our lattice model also provides a generic insight into aggregation and its predictions can be readily applied to any HCSS-like pair potential. A nice feature of the theory, by virtue of its likeness to the Ising model, is its special symmetry under toggling occupied and unoccupied sites at half-filling, which gives us a way to understand the existence of the inverse phases[3]. But like the related density-functional theory approaches [17,18] the lattice model is less convenient for the analysis of the detailed morphology of the possible aggregate phases, and it fails to distinguish ordered from disordered states in the aggregates. To this end, we study the 2D HCSS system off-lattice by constructing a mean-field model which captures the salient features of self-assembly. We assume that the particles are confined to the aggregates and that shape of the aggregates in each mesophase is fixed, *e.g.*, the micelles and the voids in the inverse micellar phase are circular and the lamellae are straight. Each of the mesophases is then parametrized by two structural parameters, the aggregate size and the lattice spacing, which define the effective density of particles within the aggregates relative to the average density. To estimate the free enthalpy of each phase, we ignore any positional correlations of particles between neighboring aggregates. Within this approximation, the intra-aggregate structure is the same as in a hard-disk system[4], and we calculate the entropy of the fluid and the crystalline order in the aggregates using an empirical equation of state for the hard-disk fluid [19] and the cellular theory of the hard-disk crystal [20], respectively. The average overlap energy is evaluated by summing overlaps of the spheres in a given aggregate and in neighboring aggregates. Thus we obtain the free enthalpy of the various mesophases in a closed analytic form as a function of temperature, density, and the two structural parameters, aggregate size and lattice spacing (the latter are fixed via Lagrange multipliers). An example of the resulting phase diagram of the aggregate phases, which are stable at low enough temperatures $\beta\epsilon \gtrsim 1$ and include micellar and lamellar phases with both fluid and crystalline intra-aggregate order as well as the crystalline inverse micellar phase, is shown in fig. 2. We do not find a fluid inverse micelle phase, nor is such a phase observed in the Monte Carlo simulations of the HCSS system described below.

In units of σ_s^{-1}, the wavenumber at which ordering occurs only depends weakly on the dimensionless pressure $p\sigma_s^2/\epsilon$ and is, interestingly, roughly independent of the particular phase, be it micellar, lamellar, or inverse micellar (fig. 3). This behavior recapitulates the results for a generalized exponential interaction without hard cores [16]. Taken together with the observation that the qualitative features of the phase diagram are independent of σ_s/σ, this confirms our notion that we can think of the aggregates as larger interacting particles with the internal structure only changing the effective inter-aggregate interactions. The relative unimportance of the hard-core

[3] Rewriting eq. (2) in terms of "hole" variables $n_i' = 1 - n_i$, we retain the same model (up to a constant) with a chemical potential for holes, $\mu' = -\mu + \sum_j V_{\rm SS}(\mathbf{r}_j)$.

[4] This is true as long as the aggregate size is smaller than σ_s, which was verified *a posteriori*.

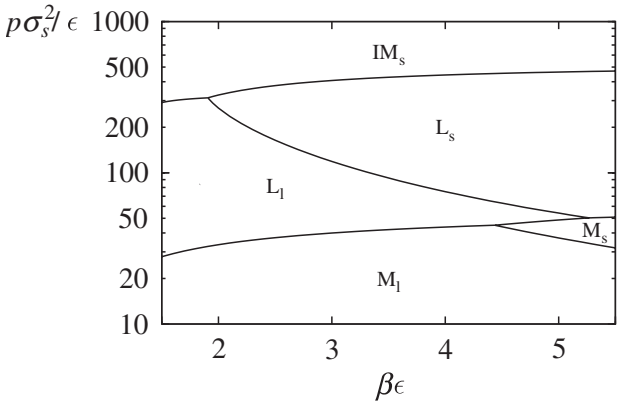

Fig. 2: Theoretical phase diagram of the modulated phases of two-dimensional hard-core/soft-shoulder particles with $\sigma_s/\sigma = 5$ includes the solid (M_s) and liquid (M_l) micelle phase, the solid (L_s) and liquid (L_l) lamellar phase, and the solid inverse micelle phase (IM_s). Phase boundaries were calculated using the off-lattice model; $p\sigma_s^2/\epsilon$ is the reduced pressure and $\beta\epsilon$ is the reduced inverse temperature.

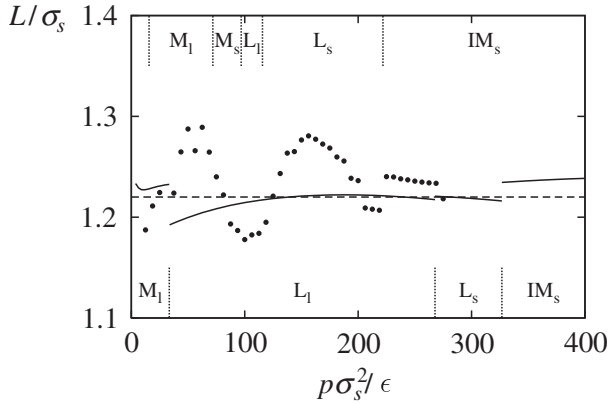

Fig. 3: Wavelength of principal mode *vs.* pressure for $\sigma_s/\sigma = 5$ and $\beta\epsilon = 2$. The dashed line shows the prediction from the lattice, mean-field theory, $L/\sigma_s \simeq 1.22$; the solid line shows the results of the mean-field, off-lattice calculation with the boundaries of the respective phases labeled below; and the filled circles show the results from the simulations with the phases labeled above. The phase morphologies are labeled as in figs. 1 and 2. The lattice constant and the wavelength differ by a multiplicative factor of $\sqrt{3}/2$ in the hexagonal phases.

interaction arises when the aggregates are large and an additional sphere can be accommodated without requiring a large rearrangement of the internal structure. Our analysis corroborates the results of Monte Carlo (MC) simulations of the HCSS system at fixed N, p, and T [21]. At low temperatures, the MC simulations reveal a series of first-order transitions, with decreasing pressure, from crystalline inverse micelles, to crystalline lamellae, to liquid lamellae, to crystalline micelles, to liquid micelles, to isotropic micellar liquid, in qualitative agreement with the phases and phase diagram of our mean-field treatment. However, the simulations offer a much more detailed insight into the structure of the mesophases as they are free of the limitations of the mean-field model[5], and they predict several distinct structural variants of each type of phase, *e.g.*, between different crystalline lamellar phases. A complete discussion of the simulation results will appear elsewhere [21].

To understand the unwavering magnitude of the wave vector within the off-lattice model, we focus on the average overlap energy of the particles in the lamellar phase. For $\ell < \sigma_s$ the lowest-order approximation of the cumbersome but analytical form of the intra-lamellar interaction reads $E_{\rm intra} \approx \epsilon\rho(\ell + a)\sigma_s$, where a is the width of the gaps between the lamellae and thus the centers of the lamellae are $L = \ell + a$ apart; $\rho_{\rm eff} = \rho(\ell + a)/\ell$ is the effective density of particles in the lamellae. This result can be understood by noting that for $\ell < \sigma_s$, each particle within a lamella overlaps with about $2\ell\sigma_s\rho_{\rm eff}$ neighbors. The intra-lamellar interaction is an increasing function of both a and ℓ, and fixing the lattice constant amounts to fixing the energy per particle due to intra-aggregate interactions. On the other hand, the inter-lamellar repulsion decreases both with a and ℓ: As a grows for fixed ℓ, fewer particles in neighboring lamellae interact, and, as ℓ grows for fixed a, the fraction of the particles at the edge of each lamella which overlap more strongly with the neighboring lamella is reduced. To lowest order, the inter-lamellar interaction predicted by the off-lattice model is $E_{\rm inter} \approx 0.75\epsilon\rho\sqrt{\sigma_s}(\sigma_s - a)^{5/2} \times (\ell + a)/\ell^2$, which like $E_{\rm intra}$ has a simple geometric origin. Only particles within a surface layer of width $\sigma_s - a$ interact with particles on a neighboring cluster. The average number of particles a given surface particle reaches grows as $\sigma_s^{1/2}(\sigma_s - a)^{3/2}\rho_{\rm eff}$, while the fraction of particles at the surface is $(\sigma_s - a)/\ell$. The minimum of $E_{\rm inter} + E_{\rm intra}$ (subject to the condition that $\rho_{\rm eff}$ should not exceed the close-packed density $2/\sqrt{3}\sigma^2$) indeed lies on the line $\ell + a \approx 1.2\sigma_s$. We also find that the equilibrium value of ℓ is as small as allowed by this condition, as if the lamellae were being compactified by an effective surface tension arising from the inter-lamellar repulsion.

In conclusion, we have shown that particles interacting with a simple, isotropic and purely *repulsive* interaction can nevertheless display a wealth of complex mesophases. These phases arise quite generically from a large class of interaction potentials whose Fourier transforms have negative regions. We note that the observed phase sequence is analogous to the ordered phases of diblock copolymers [22] and amphiphiles in water [23] despite the isotropic symmetry of the interaction. Near the critical point of the molten copolymer, quite generic Landau-theory considerations lead to the diversity of modulated structures

[5] In the off-lattice model, we neglect the inter-aggregate positional correlations of colloids, which are most prominent in the crystalline variants of the aggregate phases. These correlations may affect the shape and the structure of the aggregates and thus the free energy of the phase in question. This is likely the main reason for the quantitative discrepancy between the theoretical phase diagram and the MC simulations.

in equilibrium [24]. We expect the mean-field theory of hard-core/soft-shoulder colloids to be very similar to the copolymer theory, which suggests that in three dimensions such systems can be expected to form lattices of spherical, cylindrical, and lamellar aggregates as well as their inverses and the bicontinuous gyroid phase.

Our model can be further generalized by including a short-range attraction in addition to a long-range repulsion [17,25]. Though the details would be different, our conclusion of an ordering instability would remain and the same qualitative arguments would still hold as the aggregation phenomenon is encoded in the Fourier transform of the soft part of the pair potential. Our analysis also suggests that the morphological similarities between repulsive self-assembly and clustering due to competing short-range attraction and long-range repulsions [26] are more than superficial: they reflect the common structure of the Fourier transform of the interaction potential. From the point of view of our off-lattice calculation, however, it is quite difficult to understand whether repulsive self-assembly truly represents the same mechanism as clustering due to competing interactions. It would be interesting to resolve this issue in the future.

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