Microphase separation in a two-dimensional colloidal system with competing attractive critical Casimir and repulsive magnetic dipole interactions

Kevin Marolt,* Michael Zimmermann, and Roland Roth
Institute for Theoretical Physics, University of Tübingen,
Auf der Morgenstelle 14, 72076 Tübingen, Germany
(Dated: November 27, 2019)

We propose and study theoretically a novel colloidal system in two dimensions with attractive critical Casimir and repulsive magnetic dipole forces, wherein the strength of attraction and repulsion can be easily and independently tuned by adjusting the temperature and an external magnetic field, respectively. We expect this setup to be experimentally accessible and are confident that it can serve to deepen our understanding of the mechanisms behind microphase separation due to competing interactions. We develop a density functional theory for our model and present first results of our calculations in the form of a phase diagram for fixed temperature, but varying magnetic fields and bulk densities. For certain values of these parameters, we are able to confirm the existence of thermodynamically-stable inhomogeneous density profiles in the bulk, such as parallel lamellar stripes, as well as clusters and voids on a hexagonal lattice.

I. INTRODUCTION

One of the more fascinating phenomena that a wide variety of two- and three-dimensional soft matter systems exhibit is the emergence of thermodynamically-stable, periodic density fluctuations in the bulk, i.e., in the absence of any external forces. Example of these so-called microphases are lamellar patterns with alternating parallel stripes or sheets of higher and lower density, and dense circular or spherical clusters on a regular lattice [1]. There exist multiple mechanisms that can cause these highly-ordered structures. Take, for instance, diblock copolymers, which are covalently-bound pairs of monomers of different species. If the two species are immiscible to each other, the monomers segregate at sufficiently low temperatures, developing domains of one monomer type that necessarily border on domains of the other type. The morphology and length scale of these structures depend on the composition and length of the monomers [2, 3], and are in this case the consequence of the orientation-dependent forces between the copolymers.

What might be somewhat surprising, however, is that such spatial inhomogeneities can also be observed in systems with isotropic interactions, as is demonstrated by Langmuir monolayers of amphiphilic molecules [4, 5]. These molecules possess a polar, hydrophilic “head” and an apolar, lipophilic “tail”. When they are brought onto a flat air-water interface, their heads are drawn towards the water, whereas as their tails are rejected by it, so that the amphiphiles align themselves perpendicular to the interface, with tails exposed to the air. While the tails feel an attraction towards each other over short distances as a result of van der Waals forces, the heads are repelled due to dipolar repulsion even at larger separations. Although these competing interactions are radially symmetric within the molecular film, they can induce microphase separation if they are balanced just right: then, the short-ranged attractions allow local agglomerations of molecules to form that are, as a whole, driven apart by the longer-ranged repulsion.

Remarkably, the phase diagrams of such self-assembling systems [6–8] all turn out to be very similar and, as Ciach et al. [9, 10] were able to show, display the same universal sequence of microphases for increasing bulk densities, regardless of the specific interaction between the particles.

Considerable experimental and theoretical effort has been put into realizing and studying competing interactions within colloidal systems. In view of their versatility and comparative simplicity, there were expectations that further insight into the physics behind microphase separation could be gained. But while Monte Carlo simulations [11, 12] and density functional theory calculations [13, 14] indeed showed that colloids – modeled as hard spheres under the influence of an attractive and a repulsive Yukawa potential – are able to replicate the structures formed by diblock copolymers and amphiphilic Langmuir layers, experiments – usually featuring a combination of attractive van der Waals, capillary or depletion forces in competition with the repulsive electrostatic interaction of the charged colloids – have proved less successful so far. Although the aggregation of irregular clusters and the assembly of intricate foam- or gel-like networks could be observed [15–18], ordered periodic structures failed to manifest themselves. The reasons for this remain unclear; Royall suspects a “breakdown in the idea that a simple summation of the attractive and repulsive components will describe the system” when the aforementioned interactions are put together [19].

The current state of affairs being as it is, there is clearly a need to bring theory and experiment into unison. It is our hope to pave the path toward this goal by proposing a model system that incorporates magnetic dipole repulsion and critical Casimir attraction into a colloidal monolayer. We point out that the individual building

* kevin.marolt@uni-tuebingen.de
blocks are by no means novelties: both colloids subject to magnetic dipole interactions [20, 21] as well as those experiencing critical Casimir forces [22, 23] have already been successfully realized in experiments and were found to agree exquisitely with theoretical predictions. We expect that a combination of the two can be readily put into practice, but are unaware of any studies that have yet attempted such an endeavor.

The strength of the magnetic dipole and critical Casimir forces can be tuned via an external magnetic field and the temperature, respectively. On the one hand this is a blessing, because one is able to easily adjust the repulsive and attractive interaction independently from each other by turning two extrinsic control knobs – and it should be interesting to see how the shape of the resulting potential affects microphase separation in the system. On the other hand, the large parameter space can also be a curse, as it seems futile to guess which choice of magnetic field, temperature and bulk density might result in interesting behavior. This is especially problematic for experimentalists, whose work tends to be so expensive and time-consuming that some guidance from prior theoretical analysis would surely be welcome.

In this paper, we shall give a detailed overview of our proposed system in Sec. II, derive a density functional theory for the model in Sec. III and present some very promising first findings in Sec. IV. In Sec. V we draw our conclusion.

II. THE MODEL

Consider a single layer of electrostatically charged, superparamagnetic colloids with diameter $a$ immersed in a binary liquid mixture on top of a planar surface immersed in an external magnetic field perpendicular to it. Due to screening effects, the electrostatic forces decay exponentially with the Debye screening length $\kappa^{-1} \ll a$ as the distance between the colloids increases, effectively giving rise to a hard core with diameter $d > a$.

The external magnetic field induces a magnetic dipole moment of magnitude $M = \chi_{\text{eff}} B$ within the colloids, proportional to their effective magnetic susceptibility $\chi_{\text{eff}}$ and the field strength $B$. Because the dipoles point in the direction of the field, they are all parallel and repel each other. The magnetic dipole-dipole interaction potential is given by [20]

$$V_{\text{mag}}(r) = \frac{\mu_0 M^2}{4\pi r^3} = \frac{\mu_0 \chi_{\text{eff}}^2 B^2}{4\pi r^3},$$

where $\mu_0$ is the vacuum permeability and $r$ the center-to-center distance between two colloids.

The colloids are specifically chosen or processed in such a way that they preferentially adsorb one or the other of the solvent’s constituent substances. Upon approaching the critical demixing temperature $T_c$ of the solvent, the increasing concentration fluctuations within the solvent become confined between adjacent colloids and lead to a so-called critical Casimir force that pulls the particles together. The range and strength of this attraction first and foremost depends on the solvent’s bulk correlation length, which diverges as $\xi(T) = \xi_0 |(T - T_c)/T_c|^{-0.63}$ in the limit $T \rightarrow T_c$. The critical Casimir interaction between two colloids is described by the potential [23]

$$V_{\text{cas}}(r) = \frac{k_B T}{4} \frac{a}{r - a} \theta \left( \frac{r - a}{\xi(T)} \right).$$

The scaling function $\theta$ [24, 25] vanishes exponentially for large arguments and is plotted in Fig. 1 alongside the function $x \mapsto \theta(x)/x = (4/a)\xi(T)V_{\text{cas}}(x\xi(T) + a)/(k_B T)$, showing that $V_{\text{cas}}$ is indeed an attractive potential. Note that because the Casimir force between two colloids grows infinitely strong as their proper surfaces come into contact at $r = a$, the electrostatically-induced effective hard core interaction between the colloids with hard core diameter $d > a$ is required to prevent them from sticking together.

The experimental setup we propose – see Fig. 2 – is essentially the merging of the one described by Zvyagolskaya et al. [23, 26] with that of Bubeck et al. [21]. It consists of spherical silica colloids with a paramagnetic core, that are a few microns in diameter and submerged in a water–2,6-Lutidine mixture. This suspension is confined to a temperature-controlled glass cell in which the sol-
loids sediment toward the bottom under the force of gravity and form a flat monolayer (provided that the mass of the colloids is sufficiently high so that variations of their height due to thermal fluctuations are negligible). The cell is then placed inside the homogeneous magnetic field of, say, a copper coil, such that the field is perpendicular to the monolayer. Because silica and glass surfaces in contact with an aqueous solution acquire a negative surface charge [27], the colloids and the cell become hydrophilic, thus preferably adsorbing water. This not only increases the (one-particle) density distribution \( \rho \), but also leads to a repulsive critical Casimir force between the colloids. Of course, the same interactions also occur between the nearby particles. In the center of the cell – given that the cell is large enough – the system should therefore only show small deviations from bulk behavior.

All calculations in this paper pertain to colloids with \( a = 3 \mu m, d = 3.1 \mu m [23] \) and \( \chi_{\text{eff}} = 7.62 \text{Am}^2\text{T}^{-1} [20] \), immersed in a binary mixture with \( T_c = 307 \text{K} \) and \( \xi_0 = 0.2 \text{nm} [22] \). The competing interaction potential \( V_{ci} = V_{mag} + V_{cas} \) is presented in Fig. 3 for different combinations of \( B \) and \( T \). Filled circles mark the maxima of \( V_{ci} \). Fig. 3a shows how the potential changes if either the magnetic field or the temperature is varied, whereas Fig. 3b demonstrates that one can, e.g., precisely set the location \( r^* \) and height \( V_{ci}(r^*) \) of the maximum by choosing appropriate values of \( B \) and \( T \). If, additionally, the diameters \( a \) or \( d \) could be varied, even more possibilities would open up.

Having established that \( V_{ci} \) clearly has all the trademarks of a competing interaction potential, we will now continue with the development of a density functional theory to determine whether microphase separation can occur in our system.

### III. Density Functional Theory

For a grand-canonical ensemble with chemical potential \( \mu \), there exists a unique functional \( \rho \to \Omega_{\mu}[\rho] \) of the (one-particle) density distribution \( \rho \) that is equal to the grand potential \( \Omega_{\mu} \) when evaluated for the equilibrium density distribution \( \rho_{eq} \), and strictly larger than \( \Omega_{\mu}[\rho_{eq}] \) for any other non-equilibrium density distribution \( \rho_{ne} \neq \rho_{eq} [28] \):

\[
\Omega_{\mu} = \Omega_{\mu}[\rho_{eq}] < \Omega_{\mu}[\rho_{ne}].
\] (3)

In the absence of an external potential, the grand potential functional is given by

\[
\Omega_{\mu}[\rho] = \mathcal{F}[\rho] - \mu \int_V d^2r \rho(r),
\] (4)

where \( V \) is the system volume and \( \mathcal{F} \) the Helmholtz free energy functional. Note that, although our model system is of course three-dimensional in reality, the thermodynamics are effectively two-dimensional because the colloids are confined to a single flat plane. As such, all of the following calculations are for a two-dimensional system. This means that, e.g., the volume \( V \) is actually a surface area, \( \rho \) denotes the number of particles per unit area and that the colloids are treated as hard disks.

It proves practical to write \( \mathcal{F} \) as the sum of an ideal gas part \( \mathcal{F}_{id} \), an excess hard disk part \( \mathcal{F}_{hd}^\text{ex} \), and an excess competing interactions part \( \mathcal{F}_{ci}^\text{ex} \): \( \mathcal{F} = \mathcal{F}_{id} + \mathcal{F}_{hd}^\text{ex} + \mathcal{F}_{ci}^\text{ex} \). The free energy functional for the ideal gas is exactly known [29] to be

\[
\beta \mathcal{F}_{id}[\rho] = \int_V d^2r \phi_{id}(\rho(r))
\] (5)

with \( \beta = (k_B T)^{-1}, \phi_{id}(\rho) = \rho [\ln(\Lambda^2 \rho) - 1] \) and the thermal wavelength \( \Lambda [30] \). For the hard disk part, we employ an accurate functional that has been derived in Ref. [31] with inspirations from fundamental measure theory. It is given by

\[
\beta \mathcal{F}_{hd}^\text{ex}[\rho] = \int_V d^2r \phi_{hd}(n(r, \rho)),
\] (6)
where \( \phi_{\text{int}} \) is a function of a set \( \mathbf{n} \) of so-called weighted densities, with each element \( \mathbf{n}_\alpha \) defined as the convolution of the density distribution \( \rho \) with a corresponding weight function \( \omega_\alpha \),

\[
\mathbf{n}_\alpha(\rho, \mathbf{r}) = \int d^2 r' \rho(\mathbf{r'}) \omega_\alpha(\mathbf{r} - \mathbf{r'})
\]

[32]. Finally, to incorporate the critical Casimir and magnetic interactions, we use the random phase approximation (RPA)

\[
F_{\text{cl}}^\rho = \frac{1}{2} \int_V d^2 r \int_V d^2 r' \rho(\mathbf{r}) \rho(\mathbf{r}') V_\rho(\mathbf{r} - \mathbf{r}')
\]

(7)

with

\[
V_\rho(r) = \begin{cases} 
V_{\text{cs}}(d) + V_{\text{mag}}(d) & \text{if } r \leq d, \\
V_{\text{cs}}(r) + V_{\text{mag}}(r) & \text{otherwise,}
\end{cases}
\]

(8)

where the potential is artificially extended into the hard core to empirically correct for the systematic underestimation of correlations with RPA [33].

The existence of a minimum of the grand potential functional with a non-uniform equilibrium density distribution would prove that the system indeed exhibits microphase separation. To perform this minimization, we used two different approaches that complement each other in terms of accuracy and speed: the quasi-exact free minimization, and an approximative Landau-type theory.

### A. Free minimization

Because the equilibrium density distribution \( \rho_{\text{eq}} \) minimizes the grand potential functional, we have

\[
0 = \beta \frac{\delta \Omega_{\mu}[\rho_{\text{eq}}]}{\delta \rho_{\text{eq}}(\mathbf{r})} = \beta \frac{\delta F_{\text{eq}}}{\delta \rho_{\text{eq}}(\mathbf{r})} - \beta \mu \\
= \ln[\Lambda^2 \rho_{\text{eq}}(\mathbf{r})] - c^{(1)}(\rho_{\text{eq}}, \mathbf{r}) - \beta \mu
\]

(9)

where \( c^{(1)}(\rho, \mathbf{r}) = -\beta \frac{\delta F_{\text{ex}}[\rho]}{\delta \rho(\mathbf{r})} \) is the one-body direct correlation function of \( F_{\text{ex}} = F_{\text{ex}}^{\text{bd}} + F_{\text{ex}}^{\text{cl}} \) [34], \( \mu_{\text{ex}}(\rho_0) = \mu - \mu_{\text{id}}(\rho_0) \) the excess chemical potential with \( \mu_{\text{id}} = \ln(\Lambda^2 \rho_0) \), and \( \rho_b = \rho^b = \frac{1}{V} \int_V d^2 r \rho(\mathbf{r}) \) the bulk density. This relation can now be recast into the self-consistency equation

\[
\rho_{\text{eq}}(\mathbf{r}) = \rho^b_{\text{eq}} \exp \left[ c^{(1)}(\rho_{\text{eq}}, \mathbf{r}) + \beta \mu_{\text{ex}}(\rho^b_{\text{eq}}) \right],
\]

(10)

which we use in the following iteration scheme to find the equilibrium density distribution: After choosing an adequate initial density profile, we generate successive density profiles by evaluating the left and right hand side of Eq. (10) for the current (non-equilibrium) density distribution \( \rho_i \) and mixing them with a suitable mixing parameter \( \alpha_i \in (0, 1) \) to obtain the successor

\[
\rho_{i+1}(\mathbf{r}) = (1 - \alpha_i) \rho_i(\mathbf{r}) + \alpha_i \tilde{\rho}_i(\mathbf{r}),
\]

(11)

where \( \tilde{\rho}_i(\mathbf{r}) = \rho^b_i \exp \left[ c^{(1)}(\rho_i, \mathbf{r}) + \beta \mu_{\text{ex}}(\rho^b_i) \right] \), such that \( \Omega_{\mu}[\rho_{i+1}] < \Omega_{\mu}[\rho_i] \) for all \( i \in \mathbb{N} \). Once this iteration has converged sufficiently close to its fixed point, we have found the equilibrium density distribution – to within some tolerance – and stop the procedure. Knowledge of the equilibrium grand potential \( \Omega_{\mu} \) as a function of the chemical potential \( \mu \) is especially useful for determining phase coexistence: If, for a given temperature \( T \), there exist two minima of \( \Omega_{\mu} \), say \( \rho^A_{\text{eq}} \) and \( \rho^B_{\text{eq}} \) with \( \rho^A_{\text{eq}} \neq \rho^B_{\text{eq}} \), that represent different phases but have the same pressure, \( P_{\mu}[\rho^A_{\text{eq}}] = P_{\mu}[\rho^B_{\text{eq}}] \) with \( P_{\mu}[\rho] = -\Omega_{\mu}[\rho]/V \), then these two states of the system can coexist.

For phase diagrams, it is more illustrative to replace the chemical potential \( \mu \) with the bulk density \( \rho_b \) or, equivalently, with the particle number

\[
N[\rho] = \rho_b V = \int_V d^2 r \rho(\mathbf{r}) = -\frac{\partial \Omega[\rho]}{\partial \mu}.
\]

As such, in order to determine the equilibrium density distribution \( \rho_{\text{eq}} \) for a given equilibrium bulk density \( \rho^b_{\text{eq}} \), we instead have to minimize the Legendre transform of \( \Omega_{\mu} \) with respect to \( \mu \),

\[
\Omega_{\mu}[\rho] - \mu \frac{\partial \Omega[\rho]}{\partial \mu} = \Omega_{\mu}[\rho] + \mu N[\rho] = F[\rho],
\]

(13)

while keeping \( \rho_b = \rho^b_{\text{eq}} \) fixed in the process. This is achieved by minimizing the modified functional

\[
F'[\rho] = F[\rho] - \gamma \left[ \int_V d^2 r \rho(\mathbf{r}) - \rho^b_{\text{eq}} V \right]
\]

(14)

with the Lagrange multiplier \( \gamma \). In equilibrium, we have

\[
0 = \beta \frac{\delta F'[\rho_{\text{eq}}]}{\delta \rho_{\text{eq}}(\mathbf{r})} = \ln[\Lambda^2 \rho_{\text{eq}}(\mathbf{r})] - c^{(1)}(\rho_{\text{eq}}, \mathbf{r}) - \beta \gamma,
\]

(15)

which can be rearranged to

\[
\rho_{\text{eq}}(\mathbf{r}) = \frac{\exp(\beta \gamma)}{\Lambda^2} \exp \left[ c^{(1)}(\rho_{\text{eq}}, \mathbf{r}) \right].
\]

(16)

Using the constraint that

\[
\rho^b_{\text{eq}} = \frac{\exp(\beta \gamma)}{\Lambda^2} \int_V d^2 r \exp \left[ c^{(1)}(\rho_{\text{eq}}, \mathbf{r}) \right],
\]

(17)

we can eliminate the factor \( \exp(\beta \gamma)/\Lambda^2 \) and arrive at

\[
\rho_{\text{eq}}(\mathbf{r}) = \rho^b_{\text{eq}} \frac{\tilde{\rho}_{\text{eq}}(\mathbf{r})}{\rho^b_{\text{eq}}},
\]

(18)

with \( \tilde{\rho}(\mathbf{r}) = \rho_b \exp[c^{(1)}(\rho_{\text{eq}}, \mathbf{r})] \) for some density distribution \( \rho \). This implies the recurrence relation

\[
\rho_{i+1}(\mathbf{r}) = (1 - \alpha_i) \rho_i(\mathbf{r}) + \alpha_i \tilde{\rho}_i(\mathbf{r})
\]

(19)

with mixing parameter \( \alpha_i \in (0, 1) \) to generate a series of density distributions with \( F[\rho_{i+1}] < F[\rho_i] \) and \( \rho^b_i = \rho^b_{\text{eq}} \).
for all \(i \in \mathbb{N}\). If, for a given temperature \(T\) and equilibrium density \(\rho^0\), there exist multiple minima of the Helmholtz free energy \(F\), then the lowest one represents the thermodynamically stable phase.

We minimize \(\Omega\) and \(F\) numerically on a workstation, with density distributions discretized on a finite regular grid of \(N_x \times N_y\) lattice points located at \(r_{ij} = (iL_x/N_x, jL_y/N_y)\) with \(i \in \{0, \ldots, N_x\}\) and \(j \in \{0, \ldots, N_y\}\). Since many computation steps involve rather expensive convolutions (e.g., \(F_{\text{eq}}\), \(n_a\), and \(c^{(1)}\)), employing the Fast Fourier Transform algorithm in conjunction with the convolution theorem and performing the calculations in Fourier space leads to a dramatic speed-up—especially when the parallel computing facilities of modern graphics processing units are harnessed [35]. Note that, because we are dealing with periodic density fluctuations, it is sufficient—and also the most efficient—to perform the minimization only for a single unit cell of those structures. This, however, introduces the unit cell volume \(V_{\text{u}}\) as another variable with respect to which \(\Omega\) and \(F\) also need to be minimized. We do this with a golden section search [36]. When density functional calculations are only done for a single unit cell, one needs to ensure that its interactions with all the other unit cells are properly accounted for. Fortunately, because our algorithm is operating in Fourier space and we use the Fourier transform of the full (non-truncated) interaction potential, this is automatically the case.

**B. Landau-type theory**

While the free minimization is able to produce very accurate results if the underlying grid is fine enough, it can take a long time to converge, and its implementation is rather complicated and error-prone. For this reason, we initially studied our system with a Landau-type theory [9, 37] that is only approximative, but in return much cheaper. One advantage of using two completely different methods was the ability to cross-check the plausibility of our results; another was that the Landau-type theory allowed us to conduct a quick but robust search for interesting regions in parameter space, which could then be refined by free minimization.

If a density distribution \(\rho\) deviates from its bulk density \(\rho_0\), i.e., \(\Delta \rho \neq 0\) for \(\Delta \rho(r) = \rho(r) - \rho_0\), then the Helmholtz free energy density can be written as \(F[\rho] = F[\rho_0] + \Delta F[\rho]\), where the perturbation term \(\Delta F[\rho]\) can be obtained via a functional Taylor expansion of \(F\) around the bulk density \(\rho_0\).

\[
\Delta F[\rho] = \sum_{n=1}^{\infty} \frac{1}{n!} \int_V d^2r_1 \cdots \int_V d^2r_n \Delta \rho(r_1) \cdots \Delta \rho(r_n) \times \left. \frac{\delta^n F[\rho]}{\delta \rho(r_1) \cdots \delta \rho(r_n)} \right|_{\rho=\rho_0}. \tag{20}
\]

In the following, we will specifically consider inhomogeneities of the form

\[
\Delta \rho(r) = \sum_{s=1}^{\sigma} \Phi_s g_s(r) = \sum_{s=1}^{\sigma} \Phi_s \sum_{k \in K_s} g_k \exp(i k \cdot r), \tag{21}
\]

where \(g_s(r) = \sum_{k \in K_s} g_k \exp(i k \cdot r) \in \mathbb{R}\) is the Fourier series over a set \(K_s\) of wave vectors henceforth referred to as the \(s\)-th shell in Fourier space, and \(\Phi_s \in \mathbb{R}\) is the amplitude of the contribution from that shell. Upon \(g_s\), we impose the normalization that \(\frac{1}{V_u} \int_V d^2r g_s^2(r) = \sum_{k \in K_s} |\hat{g}_k|^2 = 1\), where \(V_u = L_x L_y\) is the volume of the unit cell of the periodic structure described by \(\Delta \rho\). Additionally, we demand for every wave vector \(k \in K_s\) that also \(-k \in K_s\) and that \(|k| = k_s < k_{s+1}\), i.e., wave vectors from the same shell \(K_s\) are of equal magnitude \(k_s\) and higher shells comprise longer wave vectors. We shall restrict ourselves to the first two shells, \(s \in \{1, \ldots, \sigma\}\) with \(\sigma = 2\), and focus on lamellar and hexagonal density fluctuations given, respectively, by

\[
g_{\text{lam}}(x, y) = \sqrt{2} \cos(k_{\text{lam}} x) \tag{22}
\]

with \(k_{\text{lam}} = 2\pi s/L_{\text{lam}}\) for \(s \in \{1, 2\}\), and

\[
g_{\text{hex}}(x, y) = \sqrt{\frac{8}{3}} \cos\left(\frac{\sqrt{3} k_{\text{hex}} x}{2}\right) \cos\left(\frac{k_{\text{hex}} y}{2}\right)
+ \sqrt{\frac{2}{3}} \cos(k_{\text{hex}} y) \tag{23}
\]

for \(s \in \{1, 2\}\) with \(k_{1,\text{hex}} = 4\pi/L_{\text{hex}}\) and \(k_{2,\text{hex}} = 4\pi/L_{\text{hex}}\), where \(L_{\text{hex}} = \sqrt{3} L_{\text{hex}}\).

For the ideal gas, the bulk term evaluates to \(\beta F_{\text{id}}[\rho_0]/V = \phi_{\text{id}}(\rho_0)\), whereas for the perturbation term one finds

\[
\beta \frac{\Delta F_{\text{id}}[\rho]}{V} = \frac{1}{2} \rho_0 - 1 \sum_{s=1}^{\sigma} \Phi_s^2
+ \sum_{n=3}^{\infty} \frac{1}{n!} \sum_{n_1=0}^{n} \cdots \sum_{n_\sigma=0}^{n} \Phi_s^{n_1} \cdots \Phi_s^{n_\sigma} A_{n_1, \ldots, n_\sigma}^{\text{id}} \tag{24}
\]

with coefficients

\[
A_{n_1, \ldots, n_\sigma}^{\text{id}} = \frac{n!}{n_1! \cdots n_\sigma!} \phi^{(n)}_{\text{id}}(\rho_0) \sum_{(k_1, \ldots, k_n) \in K_{n_1, \ldots, n_\sigma}} \hat{g}_{k_1} \cdots \hat{g}_{k_n} \tag{25}
\]

for \(n_1 + \cdots + n_\sigma = n\), where \(\phi^{(n)}_{\text{id}}(\rho) = d^n \phi_{\text{id}}(\rho)/d\rho^n\) and

\[
K_{n_1, \ldots, n_\sigma} = \left\{(k_1, \ldots, k_n) \in \prod_{s=1}^{\sigma} K_s^{n_s} : \sum_{i=1}^{n_s} k_i = 0\right\}. \tag{26}
\]

The excess hard disk contribution in the bulk is \(\beta F_{\text{ex}}[\rho_0]/V = \phi_{\text{ex}}(\mathbf{n}^{\text{ib}})\), where \(\mathbf{n}^{\text{ib}} = n(\rho_0, \mathbf{r})\) is independent of \(\mathbf{r}\). For the deviation from the bulk, one arrives
at

\[ \beta \frac{\Delta F_{\text{ext}}[\rho]}{V} = -\frac{1}{2} \sum_{s=1}^{\sigma} \Phi_s^2 s_{b,hd}(k_s) \]

\[ + \frac{1}{n!} \sum_{n=3}^{\infty} \frac{1}{n} \sum_{n_1=0}^{\infty} \cdots \sum_{n_\sigma=0}^{\infty} \Phi_{n_1} \cdots \Phi_{n_\sigma} A_{n_1,\ldots,n_\sigma}^{\text{hd}}, \]

with \( s_{b,hd}(k) = -\sum_{\alpha_1,\alpha_2} \phi_{b,hd}^{(\alpha_1,\alpha_2)}(n^b) \tilde{\omega}_{\alpha_1}(k) \tilde{\omega}_{\alpha_2}(-k) \)

(for any wave vector \( k \) with \( |k| = k \)) being the Fourier transform of the hard disk bulk direct pair correlation function, and coefficients

\[ A_{n_1,\ldots,n_\sigma}^{\text{hd}} = \frac{n!}{n_1! \cdots n_\sigma!} \sum_{\alpha_1} \cdots \sum_{\alpha_\sigma} \phi_{\alpha_1,\ldots,\alpha_\sigma}^{(b,hd)}(n^b) \]

\[ \times \sum_{(k_1,\ldots,k_\sigma) \in K_{n_1,\ldots,n_\sigma}} \hat{g}_{k_1} \cdots \hat{g}_{k_\sigma} \tilde{\omega}_{\alpha_1}(k_1) \cdots \tilde{\omega}_{\alpha_\sigma}(k_\sigma), \]

where \( \phi_{\alpha_1,\ldots,\alpha_\sigma}^{(b,hd)}(n) = \partial^n \phi_{bd}(n)/(\partial n_{\alpha_1} \cdots \partial n_{\alpha_\sigma}) \) and \( \tilde{\omega}_\alpha \) is the Fourier transform of the weight function \( \omega_\alpha \).

As for the excess competing interactions contribution, one has \( F_{\text{ext}}^{\alpha_i}[\rho_b]/V = \frac{1}{2} \rho_b^2 \tilde{V}_{ci}(0) \) in the bulk and

\[ \beta \frac{\Delta F_{\text{ext}}^{\alpha_i}[\rho]}{V} = -\frac{1}{2} \sum_{s=1}^{\sigma} \Phi_s^2 \hat{s}_{b,ci}(k_s) \]

for the perturbation, where \( \tilde{V}_{ci} \) is the Fourier transform of the competing interaction potential, and \( \hat{s}_{b,ci} = -\beta \tilde{V}_{ci} \) that of its corresponding bulk direct pair correlation function.

Putting everything together, we arrive at

\[ \beta \frac{\Delta F[\rho]}{V} = \beta \frac{F[\rho_b]}{V} + \frac{1}{2} \rho_b^2 \sum_{s=1}^{\sigma} \Phi_s^2 \]

\[ + \frac{1}{n!} \sum_{n=3}^{\infty} \frac{1}{n} \sum_{n_1=0}^{\infty} \cdots \sum_{n_\sigma=0}^{\infty} \Phi_{n_1} \cdots \Phi_{n_\sigma} A_{n_1,\ldots,n_\sigma}^{\text{hd}}, \]

with \( \beta \frac{F[\rho_b]}{V} = \phi_{b,hd}(n^b) + \phi_{b,hd}(n^b) + \frac{1}{2} \rho_b^2 \beta \tilde{V}_{ci}(0) \), coefficients \( A_{n_1,\ldots,n_\sigma}^{\text{hd}} = A_{n_1,\ldots,n_\sigma}^{\text{hd}} + A_{n_1,\ldots,n_\sigma}^{\text{hd}} \), and the static structure factor \( S(k) = [1 - \rho_b (\hat{c}_{b,hd}^{(2)}(k) + \hat{c}_{b,ci}^{(2)}(k))]^{-1} \).

For a given temperature \( T \), magnetic field \( B \), and density \( \rho_b \), we use this expansion of the free energy density up to fourth order in \( \Delta \rho = \Phi_1 g_1 + \Phi_2 g_2 \) to numerically minimize it first with respect to \( \Phi_1 \) and \( \Phi_2 \) (employing the multi-dimensional downhill simplex minimization algorithm [36]) and then with respect to \( V_b \) (again via a golden section search) for a given equilibrium bulk density \( \rho_{\text{eq}} \).

**** RESULTS

Putting the aforementioned methodology into practice, we have produced two phase diagrams of our system for fixed temperature \( T = T_e - 0.18 \) K, magnetic field strengths \( B \) in the range \([4 \mu T, 6.5 \mu T]\) and hard disk packing fractions \( \eta_b \) for the interval \([0.1, 0.35]\). One phase diagram was obtained via the Landau route and is displayed in Fig. 4a, while another resulted from free minimization and is shown in Fig. 4b.

Both phase diagrams confirm that there indeed exist combinations of \( B \) and \( \eta_b \) for which an inhomogeneous
density profile minimizes the free energy and is therefore thermodynamically stable.

The so-called \( \lambda \)-line drawn in Fig. 4 marks the points where the static structure factor \( S \) develops a singularity (with changing sign) at some non-zero critical wave number \( k_c \), i.e., \( S(k) \rightarrow \pm \infty \) for \( k \rightarrow k_c \neq 0 \) [38]. Outside the region enclosed by the \( \lambda \)-line, \( S \) is strictly positive; inside, on the other hand, \( S \) is negative for some wave numbers \( k \). According to Eq. (30), we can always construct a non-uniform density distribution with a lower free energy density than that of the corresponding bulk if \( S(k) < 0 \) for some \( k \) (e.g., choose \( k_1 \) with \( S(k_1) < 0 \), \( \Phi_1 \neq 0 \) sufficiently small in magnitude, and \( \Phi_2 = 0 \)). Hence, only modulated phases should be thermodynamically stable inside the \( \lambda \)-line. This is in complete agreement with our findings.

We have looked for – and found – the three types of modulated phases shown in Fig. 5, which have also been observed in previous studies of two dimensional systems with competing interactions: a cluster phase (“hex+”) where high-density liquid droplets are arranged in a hexagonal pattern and surrounded by a low-density vapor (Fig. 5a–b); a lamellar stripe phase (“lam”) with alternating parallel regions of high and low density (Fig. 5c–d); and a bubble phase (“hex−”) with a hexagonal arrangement of low-density vaporous voids amid a high-density liquid (Fig. 5e–f). These structures appear in that specific order with increasing bulk density.

The density profiles in Fig. 5 were obtained via free minimization. Those with the same type of structure have equal bulk densities but different magnetic fields. We can see that weakening the repulsion by decreasing \( B \) leads to increased unit cell sizes, larger clusters or bubbles, and wider stripes. For instance, the clusters in Fig. 5b have a diameter of about \( 20d \) and are composed of roughly 180 particles. The features also become noticeably more pronounced, because the difference in density between liquid and vaporous domains grows while the width of the transition zone shrinks relative to the unit cell size. This explains why the phase diagram from the Landau-type theory compares very well with the one from the free minimization for \( B \gtrsim 6 \) mT, but deviates increasingly from it for lower magnetic fields: the short-scale density variations in this regime simply cannot be faithfully represented with a restriction to the first two shells.

In Fig. 6, the pressure \( P_\mu = -\Omega_\mu / V \) of the various microphases for \( T = T_c - 0.18 \) K and \( B = 5 \) mT is plotted against the chemical potential \( \mu \). The phase with the highest pressure for a given chemical potential is thermodynamically stable, and the intersection of two pres-
sure curves marks the point of coexistence of the respective phases. Since a higher chemical potential also corresponds to a higher bulk density, the sequence of stable phases for increasing chemical potential is identical to that for increasing bulk density: first clusters, then stripes, and finally bubbles. Because the bulk densities of two neighboring phases differ at coexistence, the phase transition between them is of first order. In the limit of very high or very low chemical potentials, the pressure curves of the inhomogeneous phases seem to converge down from above toward that of the flat, uniform bulk.

V. CONCLUSION

In an effort to devise a new means of studying microphase separation brought on by competing interactions, we have proposed a novel model system of colloids that are subject to attractive critical Casimir and repulsive magnetic forces. The critical Casimir forces are mediated by the solvent—a binary mixture liquid near its critical point—and their strength can be varied via the magnetic forces. The critical Casimir forces are subject to attractive critical Casimir and repulsive magnetic forces. Since these two opposing contributions are adjustable independently from each other, we are able to alter the shape of the interaction potential easily, and even imbue it with a characteristic competing quality: a strong but short-ranged attraction coupled with a weak but long-ranged repulsion.

While we expect that this system can be realized in experiments, there appears to be no reasonable chance for experimentalists to guess which temperature, magnetic field and bulk density $\rho_b$ would need to be chosen in order to induce microphase separation: the parameter space is simply too large.

We came to the conclusion that prior theoretical analysis would be required to provide some guidance. To this end, we have developed a density functional theory for our model system and solved it approximately by means of a Landau-type theory for density profiles of a specific form, as well as quasi-exactly via a free minimization. We opted for this dual-track approach because the Landau way allowed us to quickly perform a rough scan for interesting regions in parameter space that we could then refine by following the free minimization route.

Phase diagrams obtained from both methods were found to be comparable, speaking in favor of their plausibility. For suitable values of $T$, $B$ and $\rho_b$, we were able to observe thermodynamically stable microphases with periodic spatial density fluctuations on the length scale of several colloid diameters: a hexagonal cluster phase, a lamellar stripe phase and a hexagonal bubble phase.

Our theoretical analysis of the system has so far only scratched the surface and is first and foremost meant to serve as a proof of concept. We hope to have demonstrated that further investigations—especially of the experimental kind—are indeed merited, and are curious about which new insights might be gained therefrom.

The precise value of the thermal wavelength $\Lambda$ is irrelevant in our case. For convenience, we use $\Lambda = \sqrt{\pi/4d}$.


The Helmholtz free energy density from Ref. [31] for hard disks with diameter $d = 2R$ is given by

$$\phi_{hd}(\rho) = -\rho_1 \ln(1 - \rho_2) + (19\rho_3 - 5\rho_4 \cdot \rho_5)/(48\pi(1 - \rho_2)).$$

The weight functions for the corresponding weighted densities are

$$\omega_1(\rho) = \delta(R - |\rho|)/(2\pi R),$$
$$\omega_2(\rho) = \Theta(R - |\rho|),$$
$$\omega_3(\rho) = \delta(R - |\rho|),$$
$$\omega_4(\rho) = (\rho/|\rho|) \delta(R - |\rho|),$$
$$\omega_5(\rho) = ((\rho \rho)/|\rho|) \delta(R - |\rho|),$$

with $\rho \in \mathbb{R}^{2\times 2}$ and $(\rho \rho)_{ij} = x_ix_j$.


In our case, we find that $c^{(1)}(\rho, r) = c_{bd}^{(1)}(\rho, r) + c_{ci}^{(1)}(\rho, r)$ with $c_{bd}^{(1)}(\rho, r) = -\sum_\alpha \int_V d^2r' \phi^{(\alpha)}_{bd}(\rho, \rho') \omega_\alpha (r' - r)$ and $c_{ci}^{(1)}(\rho, r) = -\int_V d^2r' \rho(\rho') \beta V c_{ci}(r - r')$.


