Self-Assembly of Colloidal Superstructures in Coherently Fluctuating Fields

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(Dated: May 11, 2014)

The central goal of physics is to understand and control the forces of nature. In recent decades scientists have begun to invent ways to combine the fundamental physical forces and to generate new, effective interactions on microscopic and macroscopic scales. By utilizing effective interactions cold atoms can now be trapped and cooled, colloidal suspensions can be stabilized, and magnetic levitation has become possible. In condensed matter physics, the interplay of different attractive and repulsive forces can give rise to highly complex structures, ranging from gyroid phases in block copolymers, to labyrinthine phases in ferrofluids and nuclear pasta phases in neutron stars. Not surprisingly, every additional interaction increases the complexity of the resulting materials. But complex materials can also emerge from a single, simple to generate, effective interaction.

In this Letter we explore one of the simplest effective interactions that is able to generate complex structures. This interaction is the spatially coherent fluctuation interaction (scFI). The interaction occurs between dipolar magnetic (or dielectric) particles when a spatially uniform electromagnetic field varies in time (cf. Fig.1b). The first realization of this interaction was described by Martin et al. in a system of superparamagnetic colloids under balanced triaxial magnetic fields (BTMF) - rotating magnetic fields spinning on a cone with the magic angle $\theta_m = 54.7^\circ$. The emerging effective interaction was similar to the London-Van der Waals force, however, the structures that formed were far more intricate. Here we develop the general theoretical framework for understanding this important novel interaction, which is attracting a growing interest in the self-assembly communities. We explore how the scFI's intrinsically strong many-body interactions drive the formation of chains and membranes in systems of polarizable colloidal particles and how complex membrane pair interactions give rise to novel swelling colloidal foam states. The scFI generates complex structures (chains, membranes and foams) while the Van der Waals-like, incoherent fluctuation interaction (icFI) - only forms phase-separated lumps, or droplets, of matter within a two phase system. We discuss why these two related forces result in such different structures.

Consider dipolar magnetic (dielectric) particles such as colloidal beads without permanent moments. Here we use magnetic notation but all results apply to the electric formalism (paramagnets become dielectrics). Beads with index $i$ are placed in a spatially and temporally fluctuating magnetic (electric) field $\mathbf{B}_{0,i} = \mu_0 \mathbf{H}_{0,i}(t)$ (with $\mu_0$ the vacuum permeability). The field changes on a typical timescale $\tau_H$ fulfilling the condition $\tau_M \ll \tau_H \ll \tau_{visc}$ with $\tau_D$ the dipolar relaxation time and $\tau_{visc}$ the characteristic time for the bead's motion in the surrounding viscous fluid. Under these conditions the beads' magnetizations $\mathbf{M}_i$ are equilibrated, while their position coordinates $\mathbf{R}_i$ respond much more slowly and feel a net time-averaged force. The free energy functional $F(\mathbf{M}_i; \mathbf{H}_{0,i})$ for $N$ interacting beads with volume $V_i$ is then given by:

$$F(\mathbf{M}_i; \mathbf{H}_{0,i}) = -\frac{1}{2} \sum_{i=1}^{N} \mathbf{M}_i \cdot \mathbf{H}_{0,i}.$$ 

Note, that due to the large moments $\mathbf{m}_i = \mathbf{M}_i V_i$ of the beads with diameters $D > 1 \mu m$ we have $F \gg k_B T$ so that additional contributions of the configurational entropy can be safely neglected. The magnetization $\mathbf{M}_i = \chi_b \mathbf{H}_{i,loc}$ is given by the total local field $\mathbf{H}_{i,loc}$ and the bead susceptibility tensor $\chi_{b,i} = (1 + \hat{L}_i \chi)^{-1}$ with $\chi$ the bead's material susceptibility and $\hat{L}_i$ its demagnetization tensor. The dipolar interaction between the $i$-th and $j$-th bead is given by the dipole-dipole coupling tensor $T_{ij} = \varphi_{ij} f(b_{ij})$, with $\varphi_{ij} = \varphi(\mathbf{R}_i, \mathbf{R}_j) = V_i/V_j |\mathbf{R}_{ij}|^3$, $\mathbf{R}_{ij} = \mathbf{R}_j - \mathbf{R}_i$ and the tensor $f(b_{ij}) = 1 - 3b_{ij} \otimes b_{ij}$ (dyadic product) with the bonding unit vector $b_{ij} = \mathbf{R}_{ij}/|\mathbf{R}_{ij}|$. The local field is a superposition of external and all dipole induced fields and can be written as $\mathbf{H}_{i,loc} = \hat{\chi}_{b,i}^{-1} \sum_j \chi_{eff,i,j} \mathbf{H}_{j,0}$ in terms of the effective sus-
ceptibility tensor $\chi_{\text{eff},ij} = (\hat{\chi}_{b,i}(1 + \hat{\chi}_{b,j}T)^{-1})_{ij}$ - a $3 \times 3$ matrix for each $i,j$ - see details in [13].

In the following we study a spatially coherent excitation with the property $H_0^\alpha = H_0^\beta = C_{\alpha\beta} = \delta_{\alpha\beta}H_0^2$ (i, j = 1, ..., N; $\alpha, \beta = x, y, z$), where bar means averaging over time or over random time-dependent fields. Note that the correlation function $C_{\alpha\beta}$ comprises also the special case of BTMF - studied numerically and experimentally in [7, 8], where the field rotates along the z-axis with the frequency $\omega$, i.e. $H_0 = H_0(\sqrt{2}\cos\omega t, \sqrt{2}\sin\omega t, 1)$ [14]. After averaging of $F$ over $H_0^\alpha$ in all directions $\alpha = x, y, z$ (see details in [13]) one obtains an elegant expression for the scFI-free-energy

$$F_{\text{scFI}}(H_0, \{R_{ij}\}) = -\frac{\mu_0}{2} H_0^2 V_b \sum_{i,j} \text{Tr} \{\chi_{\text{eff},ij}\}.$$ (1)

in terms of $\text{Tr} \{\chi_{\text{eff},ij}\} = \chi_{\text{eff},ij}^{xx} + \chi_{\text{eff},ij}^{yy} + \chi_{\text{eff},ij}^{zz}$ - the trace of $\chi_{\text{eff},ij}$. As $\chi_{\text{eff},ij}$ describes the effective coupling of the $i$-th and $j$-th bead in presence of all other beads, it gives rise to many-body effects. These are crucial for the hierarchical structuring of colloids, as confirmed in numerical simulations [7, 8] and experiments [7, 8], where dimers, molecules, chains, branched chains, membranes and foams, instead of droplets and closed-packed 3D crystal structures. The elegant trace-formula Eq.(1) forms the basis for our further study of scFI systems. Note here that, in contrast to scFI - described by Eq.(1) in standard incoherently excited FI (icFI) systems, with $H_{i,0\alpha}H_{j,0\beta} = C_{i\beta} = \delta_{ij}\delta_{\alpha\beta}H_0^2$ (note the Kronecker symbol $\delta_{ij}$), the summation of $\text{Tr} \{\chi_{\text{eff},ij}\}$ in $F$ includes only $i = j$ terms, giving rise to the usual Van der Waals(VdW)-like forces, preferring the formation of simple droplets only [11]. In the following, we study first the bead-bead interaction, then the formation of chains and membranes, and finally the assembly of membranes in the form of foams in scFI systems.

**Dimer formation.** In a first step, let us consider a very dilute system. Here the pairwise bead-bead interactions should (at first glance) dominate in $F_{\text{scFI}}$. For two spherical beads with indices $i,j$, we have $L_{i\alpha} = (1/3)\delta_{i\alpha}$, $(\hat{\chi}_{b})_{i\alpha} = \chi_b \delta_{i\alpha}$ (with $\chi_b \leq 3$) and Eq.(1) gives $\text{Tr} \{\chi_{\text{eff},ij}\} = 3\chi_b(1 - \chi_b \phi_{ij}3)1/6$ + large distances $|R_{ij}| \gg V_b^{1/3}$, the interaction is a power-law $F_{\text{scFI}}^{(\text{bb})} = -(3/8\pi^2)(V_b\chi_b)^3\mu_0 H_0^2 |R_{ij}|^{-6}$ giving rise to an isotropic and short-range, attractive VdW-like force $F_{\text{bb}} \propto |R_{ij}|^{-7}$. This interesting two-body result was first obtained in the seminal papers [7, 8] and confirmed experimentally [9].

**Many-body force.** At first glance, the isotropic VdW-like two-body interaction $\propto |R_{ij}|^{-6}$ appears to favor droplet-like, bulk. However, this contradicts numerical simulations [7, 8] and experiments [7, 8], which show a clear tendency for chain and membrane formation. What is the microscopic origin of these complex structures in scFI systems? The reason hides in the specificity and the strength of the many-body interactions, which mark the real difference between scFI and icFI systems. In a typical icFI system, the 3-body interaction is described by an Axilrod-Teller-like 3-body potential $F_{A,T}^{(ijk)} = A_{ijk}|R_{ij}|^{-3}|R_{jk}|^{-3}|R_{ki}|^{-3}$, with $A_{ijk} \equiv \chi_b^3(1 + \cos \theta_j \cos \theta_k \cos \theta_l)$. Due to its weaker ($\sim \chi_b^3 R^{-6}$) scaling, it is typically small and overridden by the 2-body VdW-like interaction $\sim \chi_b^3 R^{-6}$ [10], giving rise to close packed droplets in icFI systems. In sharp contrast, in scFI systems the 3-body interaction $F_{\text{scFI}}^{(ijk)}$ scales very differently with distance, as seen from a $O(\chi_b^3 R^{-3})$ expansion of Eq.(1) - see details in [13], which gives

$$F_{\text{scFI}}^{(ijk)} = -\beta \sum_{i,j,k} 3 \cos^2 \theta_k - \frac{1}{|R_{ik}|^3 |R_{jk}|^3}$$ (2)

with $\beta = (3/64\pi^2)(\mu_0 H_0^2 \chi_b^3 V_b^3)$ and the sum running over all $k \neq i,j$ (for angles $\theta_k$ cf. Fig.1d). Remarkably, $F_{\text{scFI}}^{(ijk)}$ is of the same order as the 2-body interaction $\sim -\chi_b^3 |R_{ij}|^{-6}$. In fact, the 2-body interaction is formally contained in $F_{\text{scFI}}^{(ijk)}$ (for $k \neq i = j$) showing us the pitfall in the dimer formation section: for scFI

**FIG. 1:** a) The incoherent (Van der Waals-like) interaction icFI and b) the spatially coherent fluctuation interaction scFI are both induced by field fluctuations - but with different spatial correlations. c,d) While the 2-body forces are similar in both cases, the 3-body forces have different angular character and are longer ranged for scFI, Eq.(2). e) The phase diagram of clusters of size $N$ and material susceptibility $\chi$. The colloidal clusters are growing over time $[7, 8]$ and undergoing a transition from linear chains to membranes beyond a critical size $N_c(\chi)$.
the 2-body interactions are physically inseparable from the 3-body ones - at any $\chi_b$. Interestingly, $F_{\text{scFI}}^{(ij)}$ has a simple angular dependence explaining scFI's tendency to destroy 3D bulk structures: the $-\cos^2 \theta_k$ term favors $\theta_k = 0 \text{ or } \pi$, i.e. the colloidal chains found in the experiments [7-11].

Chains and membranes. The $-\cos^2 \theta_k$ term in the 3-body force of Eq.2 explains the initial formation of chains. To capture quantitatively their transition to membranes, higher $O(\chi^2 \varphi^2)$ terms beyond Eq.2 are necessary. It is however conceptually more instructive to take a more macroscopic approach, where dense chains/membranes are modelled by prolate/oblate ellipsoids. Here, $\chi_{\text{eff},ij}$ in Eq.1 is replaced by its shape-dependent continuum limit $\hat{\chi}(L) = \chi(1 + L\chi)^{-1}$, where $L$ is now the demagnetization tensor of the composite ellipsoidal structure with dimensions $a = b \neq c$ and volume $V = (4\pi/3)a^2c$ [12]. Here, $\chi$ is the composite material susceptibility, which is due to local field effects in the bead aggregate. In dense systems like chain and membranes one has $\chi > \chi_b$. The free-energy $F_{\text{setf}}$ is in this case given by

$$F_{\text{setf}}(H_0, L) = -\frac{1}{2} \mu_0 H_0^2 \chi \left\{ \frac{1}{L} \{ \hat{\chi}(L) \} \right\}. \quad (3)$$

In the continuum limit, when the number of beads is large ($N \gg 1$), chains become extreme prolate ellipsoids with a long semi-axis $a \sim ND$, a short semi-axis $a \sim D$ and the demagnetization factors $L_a = L_b \gg L_c \equiv L^c \sim N^{-2} \ln N$. Membranes, on the other hand, can be seen as extreme oblate ellipsoids with two identical half-axes $a = b \sim \sqrt{N}D$, $c \sim D$ and $L_c \gg L_a = L_b \equiv L^m \sim N^{-1/2}$, cf. Fig.1e. In both cases, for chains and membranes, $F_{\text{setf}}$ is dominated by the smallest demagnetization factors $\chi^m/\chi^c \to 0$. Since for membranes two demagnetization factors vanish, while for chains only one vanishes, the energy of a membrane is always smaller than that of the chain for $N \to \infty$, i.e. $E^m < E^c$. For finite $N$, the chain-membrane transition is reached on the line $N_c = N_c(\chi)$, where $E^m(N_c) = E^c(N_c)$. As seen from Fig.1e, $N_c$ grows with the material susceptibility $\chi$. For $\chi \approx 1 - 3$, we estimate $N_c \approx 10 - 20$ close to the experimental value $N_c \approx 10$ for the chain-membrane transition [9]. The agreement suggests that the continuum approach quantitatively captures the behavior for finite $N$.

Interaction of membranes. Once they emerge, what is the fate of the membranes as they continue growing? How do they interact and mutually order during growth? To answer these questions, we need the 2-membrane interaction for arbitrary membrane orientations $\mathbf{n}_{12}$ and anisotropic susceptibilities (of thin oblates) $\hat{\chi}^i_L = \chi(1 + L_i \chi)^{-1}$. For large distances ($\varphi_{12} \ll 1, |\mathbf{R}_{12}| \gg V_{12}^{1/3}$) one expands $\chi_{\text{eff},12} \approx \hat{\chi}^i_L(1 - \varphi_{12}/\hat{b}(\mathbf{b}_{12}) \chi^2(\hat{L}_i))$ and the long range interaction energy in Eq.1 reads for identical membranes (see details in [13]),

$$F_{\text{int}} = \alpha \left[ C_1^2 + C_2^2 + \frac{1}{2} C_3^2 - (1 - \gamma)C_1 C_2 C_3 - \frac{4}{|R_{12}|^3} \right], \quad (4)$$

with $\alpha = 3(1 - \gamma)\chi_{\text{max}}^2\mu_0 H_0^2 V_{12}^3/16\pi$, and $\gamma = \chi_{\text{min}}/\chi_{\text{max}}$ the ratio of the minimal/maximal eigenvalue of the membrane susceptibility tensor $\hat{\chi}(L)$. The dimensionless factors $C_1 = \mathbf{n}_1 \cdot \mathbf{b}_{12}$, $C_2 = \mathbf{n}_2 \cdot \mathbf{b}_{12}$, $C_3 = \mathbf{n}_1 \cdot \mathbf{n}_2$ reveal all the geometrical beauty of scFI: the 2-membrane interaction is angle dependent and repulsive in many configurations - see Fig.2a. Notably, for fixed $|\mathbf{R}_{12}|$, $F_{\text{int}}$ becomes minimal for the orthogonally twisted membrane orientation with $\mathbf{n}_1 \perp \mathbf{n}_2$, $\mathbf{n}_1 \perp \mathbf{b}_{12}$ and $\mathbf{n}_2 \perp \mathbf{b}_{12}$ ($C_{1/2/3} = 0$). The twisted membranes attract each other since $F_{\text{int}}^{(\text{tw})} < 0$ (up to the point of mutual contact), as in the coplanar case, yet the twisted configuration has lower energy. This interesting result should affect the kinetics of membrane formation: If two distant membranes start growing within a large distance they will rotate to a 90° position before touching. Therefore, some type of glassy state in their orientation may be kinetically favored. In other relevant configurations, such as the top, with two out of plane parallel membranes ($C_{1/2/3} = 1$) or the generic one (cf. Fig.2a), the interaction is repulsive with $0 < F_{\text{int}}^{(\text{gen})} < F_{\text{int}}^{(\text{tw})}$.

Emergence of foams. Simulations and experiments [7,8] provide empirical evidence for a hollow foam-like superstructure (cf. Fig.2b). What is the physical mechanism behind such dipolar foam formation? We have seen above that large aggregates prefer to form membranes, and that these membranes mutually interact. Specifically, when two distant membranes are stacked over each
other, they repel ($\mathcal{F}_{\text{int}}^{\text{top}} > 0$). In the opposite limit (contact distance), a simple estimate implies their preference to split as well [12]. It is this remarkable reluctance of membranes to mutually stack that in fact sets the microscopic structure of the foam: It is formed out of the thinnest possible membrane patches, whose thickness is collapsed onto the smallest available physical scale - the bead size $D$. The characteristic lateral size $a_M$ of these membrane patches, on the other hand, is set by the bead volume fraction in the container $f_V = V_B^{\text{tot}}/V \ll 1$ (with $V_B^{\text{tot}}$ the total volume of all beads and $V$ the container's volume). By assuming a cubic shelf structure as an ansatz, cf. Fig 2c, one obtains a patch size $a_M = 3D/f_V$.

**Pressure in scFI systems.** Since the membranes tend to grow, yet repel on the average, the container walls will feel a positive net pressure $p = -\partial \mathcal{F}/\partial V > 0$. The total free energy $\mathcal{F} = \mathcal{F}_{\text{self}} + \mathcal{F}_{\text{int}}$ has positive contributions from both the membrane self-energy $\mathcal{F}_{\text{self}}$ and their pairwise interactions $\mathcal{F}_{\text{int}}$. We can qualitatively mimic the foam structure [7, 8] using the simple shelf-like cubic lattice ansatz with the mesh-size $a_M$ (Fig.2c). The self-energies of finite membranes depend on their demagnetization factors $L^m$, which for the assumed simple shelf-like cubic lattice are given by $f_V$ as $L^m \approx \alpha_m f_V$ for $f_V \ll 1$ with $\alpha_m \approx 1/4$. For $\chi > 1$ and $L^m \chi < 1$ one has $\mathcal{F}_{\text{self}} \approx 0.5 \chi^2 f_V p_0 V_b^{\text{tot}}$ (from Eq[3]) with $p_0 = \mu_0 H_0^2/2$. The interaction energy $\mathcal{F}_{\text{int}} = (S/8\pi) \chi^2 f_V p_0 V_b^{\text{tot}}$ is calculated by explicitly summing over all interactions (given by Eq[1]) of a membrane with other membranes in the cubic shelf lattice, with a numeric constant $S \approx 10$ calculated by numerical lattice summation [13]. As a result the foam’s pressure is

$$p \approx \frac{1}{2} \mu_0 \chi^2 f_V^2 H_0^2.$$  

The foam’s pressure can assume notable magnitudes. For moderate volume fractions, fields and susceptibilities ($f_V \approx 5 \cdot 10^{-2}, \mu_0 H_0 \approx 20 \text{nT}$, and $\chi \approx 10$ in densely packed $Ni$-beads membranes) we obtain $p \approx 40 \text{ Pa}$. Since $p \propto H_0^2$, the pressure is very sensitive to the strength of excitation $H_0$ and can lead to remarkably strong swelling of the foam against gravity. The latter effect can be used to experimentally test Eq[3]. The equilibrium foam height $h$ is reached once the internal and the gravitational pressure balance, i.e. $p \approx \Delta \rho g f_V h$. For the density contrast $\Delta \rho \approx 8 \cdot 10^3 \text{kg/m}^3$ of water immersed $Ni$-beads [7, 8], $g \approx 10 \text{m/s}^2$, the foam will swell strongly up to $h \sim 1 \text{ cm}$. More precisely, due to gravity, $f_V$ and $p$ vary with $h$, i.e. $p(f_V) = p_{\text{max}}(1 - h/2h^0)^2$ giving the maximal height $h_{\text{max}} = 2h^0 \sim 2 \text{ cm}$.

**Conclusion.** We have studied the formation of hierarchical superstructures in dipolar particle systems driven by the spatially coherent fluctuation interaction. The pronounced many-body interactions give rise to a growth of anisotropic assemblies - chains, then membranes once a critical cluster size is reached. In a container of finite size, smaller membrane patches are formed, which, contrary to the case of attracting beads, repel on average, thus giving rise to dipolar foam structures. The foam exerts a positive pressure on the walls of the container due to the tendency of membranes to increase their surface areas as well as their mutual repulsion. The dipolar foam represents a new and intriguing state of colloidal matter, formed by a delicate interplay of an attractive local interaction and a net repulsive longer range force. Remarkably, both types of forces are born out of a single, conceptually simple interaction - the scFI (Eq[1]). Being so simple to generate, yet rich and intricate in its effects, makes it a promising tool for future applications in self-assembly and nano-science.

**Acknowledgements.** We thank A.Johner, H.Mohrbach, M.Greenall for discussions and comments.

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[14] Note that in the most general case found in literature [7, 8] the triaxial field is unbalanced and can have an arbitrary in-plane $H_{\parallel}$ and perpendicular magnitude $H_{\perp} = (H_{\parallel} \cos \omega t, H_{\parallel} \sin \omega t, H_{\perp})$ with $2H_{\perp} + H_{\parallel}^2 = H_0^2$. One can show that in this case the interaction can be linearly decomposed into a balanced triaxial field (BTMF) magic angle interaction and a residual dipole-dipole interaction along the orthogonal direction[13]. The latter is well understood while the former is new and investigated here.
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The $\chi^2$ scaling is valid for equilibrium conditions, where a detailed balance between the moments and (thermal or quantum) bath hold. The scaling for icFI switches to $\propto \chi^3$ if the fluctuating field is exogeneous (externally set) and non-equilibrium as in the present scFI case [13].

When a thick membrane (thickness $2D$, radius $R$ and volume $2V_m$) is cut into two parallel membranes (thickness $D$ and radius $R$ each) and separated to infinite distance there is a gain in the energy $\Delta F = 2F_{1m} - F_{2m} \approx -V_{2m}L\chi^2(1 - (1 + \chi)^{-2}) < 0$ for $L\chi \ll 1$, where $L \propto D^{3/2}V_{2m}^{-1/2}$. Physically, the second membrane lying above the first one is repelled to increase the local fields with respect to the thicker membrane case [13].
Coherent Fluctuation Interaction

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(Dated: May 11, 2014)

Supplementary Information

In this supplement we derive the key relations used in the main text. It turns out that the spatially coherent fluctuation interaction (scFI) as given by Eq.1 often permits rather compact and elegant calculations which directly lead to physical insights.

DERIVATION OF THE "TRACE-FORMULA" FOR SCFI (EQ. 1)

Here we first derive the central "Trace-Formula" (Eq.1) from the main text. Starting from the basic expression for the free-energy $F\{M_i,H_{i,0}\}$ in an inhomogeneous external field $H_{i,0}$ (with the bead-volume $V_b$, magnetization $M_i$) given by:

$$
(\mu_0 V_b)^{-1} F = \sum_{i=1}^{N} \left( \frac{1}{2} M_i \chi_b^{-1} M_i - M_i H_{i,0} \right) + \frac{1}{2} \sum_{i,j \neq i} M_i \hat{T}_{ij} M_j
$$

where the summation goes over $N$ beads, $\mu_0$ is the vacuum permeability and $\chi_b$ (we assume equal beads) is the bead susceptibility in external field. The dipole-dipole interaction is described by $\hat{T}_{ij} = \varphi_{ij} \hat{t}(b_{ij})$ ($i \neq j$), with $\varphi_{ij} \equiv \varphi(R_i,R_j) = V_b/4\pi |R_{ij}|^3$, $R_{ij} \equiv R_i - R_j \neq 0$ and the tensor $\hat{t}(b_{ij}) = 1 - 3 |b_{ij}| \langle b_{ij} \rangle$ (dyadic product in bra-ket form) with the "bonding" unit vector $b_{ij} = R_{ij}/|R_{ij}|$.

After minimization w.r.t. $M_i$ we obtain the equilibrium free-energy (for fixed coordinates $\{R_i\}$)

$$
F_{scDI}\{H_{i,0}\} = -\frac{1}{2} \mu_0 V_b \sum_i M_i H_{i,0}.
$$

The magnetizations $M_i = \chi_b H_{i,loc}$ are given by the total local fields $H_{i,loc}$, i.e. by the superposition of external and all dipole induced fields. These local fields are related to the imposed external fields $H_{i,0}$ via the matrix (in continuum limit integral) equation

$$
\sum_j \left( \delta_{ij} + \chi_b \hat{T}_{ij} \right) H_{j,loc} = H_{i,0}.
$$

The last line is strictly valid if we adopt the practical convention that $\hat{T}_{ii} = 0$ for two identical particle indices. The formal solution for the local fields $H_{i,loc}$ gives $\chi_b H_{i,loc} = \sum_j \chi_{eff,ij} H_{j,0}$ with the operator $\chi_{eff} = \chi_b (1 + \chi_b \hat{T})^{-1}$. Its components can be formally written as $\chi_{eff,ij} = \langle R_i| \chi_b (1 + \chi_b \hat{T})^{-1} |R_j \rangle$ where $\langle R_i| \hat{A} |R_j \rangle = A_{ij}$ stands for the components of the operator $\hat{A}$ with respect to particles $i$ and $j$. Note that each component $\chi_{eff,ij}$, for fixed $i$ and $j$, is itself a 3 dimensional 2-tensor (a $3 \times 3$ matrix in 3 dimensional space). Note also, that the $i,j$ components are to be evaluated after the operator inversion, which is at the very origin of many-body forces (cf. below).

Now, the free-energy is given by $F\{H_0,\{R_i\}\}$. Since $H_{i,0}$ is a time (and possibly position) fluctuating field, the average $F$ over fluctuations gives the average free-energy

$$
\bar{F}(H_0,\{R_i\}) = -\frac{\mu_0}{2} V_b \sum_{i,j} \bar{H}_{i,0} \chi_{eff,ij} \bar{H}_{j,0}
$$

$$
= -\frac{\mu_0}{2} V_b \sum_{i,j,\alpha,\beta} C_{ij}^{\alpha\beta} \chi_{eff,ij}^{\alpha\beta}
$$

where the field correlation function $C_{ij}^{\alpha\beta} = \bar{H}_{i,0}^{\alpha} \bar{H}_{j,0}^{\beta}$ and $\alpha,\beta = x, y, z$ and $i, j = 1, 2, \ldots N$. 

Two limiting cases for $C_{ij}^{\alpha \beta}$ are of interest:

1. The spatially coherent fluctuation interaction (scFI) with $C_{ij}^{\alpha \beta} = C^{\alpha \beta} = \delta_{\alpha \beta} H_0^2 + h^{\alpha \beta}$. The first term in $C_{ij}^{\alpha \beta}$ is the time-averaging over a statistically isotropic, spatially coherent (uniform) excitation while the second term $h^{\alpha \beta}$ describes the anisotropic contributions. The "isotropic" case (with $C_{ij}^{\alpha \beta} = \delta_{\alpha \beta} H_0^2$) is the main subject in the manuscript. The corresponding free-energy is given by

$$\tilde{F}_{scFI}(H_0, \{R_i\}) = -\frac{\mu_0}{2} H_0^2 V_b \sum_{i,j} Tr(\hat{\chi}_{eff,ij}). \tag{5}$$

where $Tr(\hat{\chi}_{eff,ij}) = \chi_{eff,ij}^{xx} + \chi_{eff,ij}^{yy} + \chi_{eff,ij}^{zz}$.

Note, the "isotropic" correlation function $C_{ij}^{\alpha \beta} = \delta_{\alpha \beta} H_0^2$ comprises also the case of balanced triaxial magnetic fields (BTMF) - studied numerically and experimentally in literature, where the magnetic field rotates with the frequency $\omega$ on the cone with the magic angle $\theta_m (= \arccos(1/\sqrt{3}) \approx 54.7^\circ)$ (with $\cos \theta_m = \sin \theta_m$). In this case we parametrize the field $H_0(t) = \sqrt{3} H_0(\sqrt{2} \sin \theta_m \cos \omega t, \sqrt{2} \sin \theta_m \sin \omega t, \cos \theta_m)$. This gives $H_0(t) = H_0(\sqrt{2} \cos \omega t, \sqrt{2} \sin \omega t, 1)$ and $H_{ij}^0 H_{ij}^0 = \delta_{\alpha \beta} H_0^2 \varepsilon_i \varepsilon_j$ i.e. indeed an isotropic interaction.

2. The spatially incoherently excited fields (different at all particle positions) - (icFI) systems, with $C_{ij}^{\alpha \beta} = \delta_{ij} C^{\alpha \beta}$, which again contains isotropic and anisotropic terms. Note the $\delta_{ij}$ term destroying correlations between excitations for different particles. In the isotropic icFI case ($C_{ij}^{\alpha \beta} = \delta_{ij} \delta_{\alpha \beta} H_0^2$) we have then:

$$\tilde{F}_{icFI}(H_0, \{R_i\}) = -\frac{\mu_0}{2} H_0^2 V_b \sum_i Tr(\hat{\chi}_{eff,ii}). \tag{6}$$

Note the difference between the two cases (1) and (2). In the incoherent case (ii) $\tilde{F}_{icFI}(H_0, \{R_i\})$ contains a summation over index $i$ only, and includes only diagonal terms $i = j$, which is analogous to the usual Van der Waals (vdW) -like forces. However in case (1) it is the double summation over $i$ and $j$ which gives rise to all interesting physics, in particular the strong many body effects characteristic of scFI.

**DERIVATION OF THE THREE-BODY FORCES FOR SCFI (EQ. 2)**

In the case of the spatially coherent fluctuation interaction (scFI) the effective free-energy is given by Eq.(1) in the paper

$$\tilde{F}_{scDI}(H_0, \{R_i\}) = -\frac{\mu_0}{2} H_0^2 V_b \sum_{i,j} Tr(\hat{\chi}_{eff,ij}). \tag{7}$$

where $Tr(\hat{\chi}_{eff,ij}) = \chi_{eff,ij}^{xx} + \chi_{eff,ij}^{yy} + \chi_{eff,ij}^{zz}$ is the trace of the effective many body susceptibility tensors $\hat{\chi}_{eff,ij}$. In the simplest case of isotropic magnetic beads with isotropic (scalar) susceptibility (with respect to the external field) $\chi_b$, one has $\hat{\chi}_{eff,ij} = \langle R_i | \hat{\chi}_{eff} | R_j \rangle = \chi_b (R_i | (1 + \chi_b \hat{T})^{-1} | R_j)$ and $\hat{\chi}_{eff} = \chi_b (1 + \chi_b \hat{T})^{-1}$ can be expanded in terms of powers of $\chi_b \hat{T}$

$$\hat{\chi}_{eff} = \chi_b \hat{T} - \chi_b^2 \hat{T} + \chi_b^3 \hat{T} - \chi_b^4 \hat{T}^3 + ... \tag{8}$$

The dimensionless free-energy $f_{scDI} = \tilde{F}_{scDI}(H_0, \{R_i\})/(\mu_0 V_b H_0^2/2) = f_1 + f_2 + f_3 + ...$ is given by

$$f_{scDI} = -\chi_b N_b + \chi_b^2 \sum_{i \neq j} \hat{T}_{ij} + \chi_b^3 \sum_{m=1}^N \sum_{i 
eq j} \hat{T}_{im} \hat{T}_{mj} + O(\chi_b^4 \hat{T}^3) \tag{9}$$

The first term $f_1 = -N_b \chi_b$ describes the self-energy of (noninteracting) beads, where $N_b$ is the number of beads. The second pairwise term (i.e. the first order dipole-dipole-like interaction) $f_2 = \chi_b^2 Tr(\hat{T}_{ij}) = 0$ is strictly zero for scFI as the operator $\hat{T}_{ij}$ is always traceless. This is easy to see, since in any orthogonal basis $\{ |e_\alpha \rangle, \alpha = x, y, z \}$ one has

$$Tr(\hat{T}_{ij}) = \varphi_{ij} Tr(\hat{\varphi}(\hat{b}_{ij})) = \varphi_{ij} \sum_\alpha \{ |e_\alpha \rangle \langle e_\alpha | - 3 \langle e_\alpha | b_{ij} \langle b_{ij} | e_\alpha \rangle \} \propto 3 - 3 = 0. \tag{10}$$
The third term $f_3$ is the first (lowest order) non-trivial one. It is very interesting since it contains the three-body interactions too. It consist of terms of the form $\langle \hat{1} + \beta \rangle \langle \hat{1} + \beta \rangle (\hat{1} - 3 \langle \hat{b}_{im} | \hat{b}_{jm} \rangle)$ which can be easily evaluated

$$-Tr \left( \hat{T}_{im} \hat{T}_{jm} \right) = - \frac{V_0^2}{4\pi^2 |R_i - R_m|^3 |R_j - R_m|^3} Tr \left[ (\hat{1} - 3 \langle \hat{b}_{im} | \hat{b}_{jm} \rangle) (\hat{1} - 3 \langle \hat{b}_{jm} | \hat{b}_{jm} \rangle) \right]$$

$$= - \frac{V_0^2}{16\pi^2 |R_i - R_m|^3 |R_j - R_m|^3} Tr \left[ (\hat{1} + 9 \langle \hat{b}_{im} | \hat{b}_{jm} \rangle | \hat{b}_{jm} \rangle (\hat{1} - 3 \langle \hat{b}_{jm} | \hat{b}_{jm} \rangle + \langle \hat{b}_{jm} | \hat{b}_{jm} \rangle \right)$$

$$= - \frac{V_0^2}{16\pi^2 |R_i - R_m|^3 |R_j - R_m|^3} (3 + 9 \langle \hat{b}_{im} | \hat{b}_{jm} \rangle)^2 - 3 (1 + 1)$$

The scalar product of the (unit) bonding vectors appearing above is nothing else but the cosine of the angles between them as seen from the $m - \ell$th particle (cf. Fig 1d main text) i.e. $\langle \hat{b}_{im} | \hat{b}_{jm} \rangle = \cos (\angle i,m,j)$. Finally, the term $\hat{F}_3$ reads

$$\hat{F}_3 = - \beta \sum_{m=1}^{N} \sum_{i,j|m} \frac{3 \langle \hat{b}_{im} | \hat{b}_{jm} \rangle^2 - 1}{|R_i - R_m|^3 |R_j - R_m|^3}$$

$$= - \beta \sum_{m=1}^{N} \sum_{i,j|m} \frac{3 \cos^2 (\angle i,m,j) - 1}{|R_i - R_m|^3 |R_j - R_m|^3}$$

with a prefactor $\beta = 3\mu_0^2 \chi_b^3 V_0^2 / (64\pi^2)$ which is nothing else but Eq.2 from the main text.

Note that for $i \neq j \neq m$ Eq.(S6) contains the three-body interaction written in Eq.(2) of the manuscript. For $i = j$ it describes the second order of the two-body interactions which are isotropic (Van der Waals-like) with $\hat{F}_3^{(i,j)} \sim 1/|R_i - R_j|^6$ (see also Eq.(S5)).

We stress that the above derivations hold for isotropic magnetic beads only, where $(\chi_b)_{\alpha \beta} = \chi_b \delta_{\alpha \beta}$. In the case of anisotropic magnetic objects (e.g. membranes as well as anisotropic beads) the leading term in $\hat{F}_{sc, \alpha \beta}$ is the first-order anisotropic dipole-dipole interaction $(1/|R_i - R_j|^3)$ and described by Eq.(4) in the manuscript. Its derivation is given below.

**DERIVATION OF THE 2-MEMBRANE INTERACTION (EQ.4)**

In the previous sections we were concerned with interactions of isotropic spherical particles whose susceptibility tensors were merely diagonal i.e. $(\chi_b)_{\alpha \beta} = \chi_b \delta_{\alpha \beta}$. In the interesting case of two interacting ellipsoids (spheroids) with orientation dependent and non-trivial susceptibility tensors $\hat{\chi}_1, \hat{\chi}_2$, the free-energy in Eq.(1) of the manuscript can be rewritten in the form

$$\hat{F}_{sc, \alpha \beta} (H_0, \{R_i\}) = - \frac{\mu_0}{2} H_0^2 V \langle \hat{\chi}_{1, \alpha \beta} + \hat{\chi}_{2, \alpha \beta} \rangle$$

where

$$\hat{\chi}_{1, \alpha \beta} = (1 - \varphi_{12}^2 \hat{\chi}_{1, \alpha \beta} \hat{\chi}_{1, \alpha \beta})^{-1} (\hat{\chi}_{1, \alpha \beta} - \varphi_{12} \hat{\chi}_{1, \alpha \beta} \hat{\chi}_{1, \alpha \beta})$$

and same for $\hat{\chi}_{2, \alpha \beta}$ by replacing $1 \rightarrow 2$. The slightly more intricate form of $\hat{\chi}_{1, \alpha \beta}$ comes now from the fact that the operator $\hat{\chi}_{12} = \hat{1} - 3 \langle \hat{b}_{12} | \hat{b}_{12} \rangle$ and the susceptibilities $\hat{\chi}_i$ don't commute any more. Expanding $\hat{\chi}_{1, \alpha \beta}$ to the first order w.r.t. $\varphi_{12}$, the interaction part of $\hat{F}_{sc, \alpha \beta} (H_0, \{R_i\}) = \hat{F}_{int} (H_0, \{R_{12}\})$ from main text simplifies to

$$\hat{F}_{int}(1,2) = \frac{\mu_0}{2} H_0^2 V \varphi_{12} Tr \{ (\hat{\chi}_{1, \alpha \beta} + \hat{\chi}_{2, \alpha \beta}) \hat{b}_{12} \hat{b}_{12} \}$$

Having in mind two identical membranes (with volume $V_m$) we consider susceptibilities $\hat{\chi}_1$ and $\hat{\chi}_2$ of two oblate spheroids, which are differently oriented in space. In terms of their own local coordinate systems (in Dirac bra-ket notation for tensors) they are given by

$$\hat{\chi}_1 = \chi_{min} \langle m_1 | n_1 \rangle + \chi_{max} (\hat{1} - \langle m_1 | n_1 \rangle$$

$$\hat{\chi}_2 = \chi_{min} \langle m_2 | n_2 \rangle + \chi_{max} (\hat{1} - \langle m_2 | n_2 \rangle)$$

References and footnotes should be added if necessary.
where the unit vectors \(\mathbf{n}_1, \mathbf{n}_2\) are the normals of the membranes 1 and 2 respectively. By using Eq. (10), and noting that \(Tr\{\hat{\chi}_1\hat{\chi}_2\} = Tr\{\hat{\chi}_2\hat{\chi}_1\}\), \(Tr\{\hat{\chi}_1\hat{\chi}_2(\mathbf{b}_{21})\langle\mathbf{b}_{21}\rangle\} = Tr\{\hat{\chi}_2\hat{\chi}_1(\mathbf{b}_{12})\langle\mathbf{b}_{12}\rangle\}\) and \(Tr\{\mathbf{n}_i\langle\mathbf{n}_j\rangle\} = \langle\mathbf{n}_i\mathbf{n}_j\rangle\) (with \(\mathbf{a} \cdot \mathbf{b} \equiv \langle\mathbf{a}\rangle\langle\mathbf{b}\rangle\) the scalar product) it follows

\[
Tr\{\hat{\chi}_1\hat{\chi}_2\} = \chi_{\text{max}}^2 [1 + 2\gamma + c_2^2(1 - \gamma)^2]
\]

\[
Tr\{\hat{\chi}_1\hat{\chi}_2(\mathbf{b}_{12})\langle\mathbf{b}_{12}\rangle\} = \chi_{\text{max}}^2 [1 - (1 - \gamma)(c_1^2 + c_2^2) + (1 - \gamma)^2c_1c_2c_3],
\]

where \(\gamma = (\chi_{\text{min}}/\chi_{\text{max}})\) and \(c_1 = \mathbf{n}_1 \cdot \mathbf{b}_{12}, \ c_2 = \mathbf{n}_2 \cdot \mathbf{b}_{12}, \ c_3 = \mathbf{n}_1 \cdot \mathbf{n}_2\) are factors describing the mutual orientation of membranes. By replacing Eqs. (17-18) in Eq. (15) (where \(V_0\) in \(\varphi_{12}\) is replaced by the membrane volume \(V_m\)) one obtains Eq. (4) in the manuscript.

**DERIVATION OF THE EQUATION OF STATE \(p(f_V)\) (EQ.5)**

Let us define the volume fraction \(f_V = (N_mV_m/V) \approx V_m^{\text{tot}}/V\) where \(V_m(\approx D a_m^3)\) is the volume of the single membrane and \(N_m\) is the total number of (equal) membranes in the container volume \(V \approx Na_m^3\), and \(V_m^{\text{tot}}\) is the total volume of the beads. Here, \(D\) is the bead diameter and \(a_m\) is the size of the single membrane - see Fig. 2c in the manuscript. It follows that \(f_V \approx 3D/a_M\). Note, that in the following we fix \(V_m^{\text{tot}} = N_mV_m\), i.e. \(V_m^{\text{tot}} = \text{const}\).

The pressure is defined by \(p = -\partial \bar{F}^{\text{tot}}/\partial V\) where \(\bar{F}^{\text{tot}} = \bar{F}^{\text{sel}} + \bar{F}^{\text{int}}\) is the total energy of the membranes, \(\bar{F}^{\text{sel}}\) is the self-energy of (non-interacting) membranes and \(\bar{F}^{\text{int}}\) is the interaction energy of membranes. Eq. 3 of the manuscript gives the energy of the single membrane while the total self-energy of \(N_m\) membranes \((V_m^{\text{tot}} = N_mV_m)\) is given by

\[
\bar{F}^{\text{tot}} = -(2\chi_{\text{max}} + \chi_{\text{min}})V_m^{\text{tot}} \frac{B_0^2}{2\mu_0}
\]

where \(\chi_{\text{max}} = \frac{\chi}{1 + L_m \chi}, \ \chi_{\text{min}} = \frac{\chi}{1 + (1 - 2L_m)\chi}\)

for simplicity, we study only the case with \(\chi \gg 1\) (note the material susceptibility fulfills \(\chi > \chi_b \leq 3\), \(\chi_b\) is the bead susceptibility with respect to the applied (external) field) and \(L_m \chi \ll 1\) (\(L_m \ll 1\)). Since a membrane is considered as an extreme oblate ellipsoid with semi-axes \(c \approx D/2, \ a = b = a_M/2\) one obtains for \(L_m \approx f_V/4\) (i.e. \(f_V \ll 1\)) - for the expression for \(L_m\) in terms of \(a, c\) see Ref. 13 of the manuscript. After a straightforward small \(L_m\) expansion one obtains

\[
\bar{F}^{\text{tot}}(V) \approx -(\text{const} + \frac{1}{2}f_V \chi^2)V_m^{\text{tot}} \frac{B_0^2}{2\mu_0},
\]

where \(\text{const}\) is independent of \(f_V\) (note, \(f_V = (V_m^{\text{tot}}/V)\) and \(V_m^{\text{tot}} = \text{const}\)).

The total interaction energy of membranes \(\bar{F}^{\text{int}}\) is

\[
\bar{F}^{\text{int}}(V) = \frac{1}{2} \sum_{i,j} \bar{F}^{\text{int}}(i,j),
\]

where the pair-interaction energy \(\bar{F}^{\text{int}}(i,j)\) is given by Eq. 4 of the manuscript - its derivation is given above. For \(\chi \gg 1\) one obtains

\[
\bar{F}^{\text{int}}(V) \approx \left(\frac{1}{8\pi}f_V \chi^2S\right)V_m^{\text{tot}} \frac{B_0^2}{2\mu_0},
\]

where the constant \(S\) is given by a sum over all membranes \(i\) in the lattice interacting with a given membrane (with index \(j\))

\[
S = \sum_{i=1, i \neq j}^{N} \left(C_1^2(i,j) + C_2^2(i,j) + \frac{1}{3}C_3^2(i,j) - C_1(i,j)C_2(i,j)C_3(i,j) - \frac{2}{3}\frac{a_M^3}{|\mathbf{R}_{ji}|^3}\right)
\]
with geometric factors \( C_1(i,j) = \mathbf{n}_i \cdot \mathbf{b}_{ij}, C_2(i,j) = \mathbf{n}_j \cdot \mathbf{b}_{ij}, C_3(i,j) = \mathbf{n}_i \cdot \mathbf{n}_j \) (also given below Eq.4 in the manuscript). For the definition of \( \mathbf{n}_{1,2} \) and \( \mathbf{b}_{12} \) see above the derivation of Eq.4. If we choose the membrane \( j \) (without restriction) arbitrarily in the \( z \)-direction, i.e. \( \mathbf{n}_j = (0,0,1) \), the lattice sum \( S \) can be practically decomposed into 3 terms

\[
S = S_x + S_y + S_z
\]
each representing the contribution of one of the 3 sublattices (in \( x \), \( y \) and \( z \) direction). By evaluating the scalar products appearing in \( C_{1/2/3}(i,j) \) at each lattice site membrane \( i \), the sub-lattice sums can be written as:

\[
S_z = \sum_{(l_x,l_y,l_z) \neq (0,0,0)} \frac{1}{(l_x^2 + l_y^2 + l_z^2)^{3/2}} \left( \frac{l_z^2}{l_x^2 + l_y^2 + l_z^2} - \frac{1}{3} \right)
\]
\[
S_x = S_y = \sum_{(l_x,l_y,l_z) \neq (0,0,0)} \frac{1}{(l_x^2 + l_y^2 + l_z^2)^{3/2}} \left( \frac{l_x^2 + l_y^2}{l_x^2 + l_y^2 + l_z^2} - \frac{2}{3} \right)
\]

where the sums run over all integer triplets \( (l_x,l_y,l_z) \) (from \(-\infty \) to \(+\infty \)) which don’t vanish all at the same time. A numerical summation of these 3 terms \( S_{x/y/z} \) gives finally a value \( S \approx 10 \).

Summing up the results above, the pressure is finally given by

\[
p = -\frac{\partial \tilde{F}_{\text{tot}}}{\partial V} = \left( \frac{1}{2} + \frac{S}{8\pi} \right) \chi^2 f_v^2 \frac{B_0^2}{2\mu_0}
\]

\[
\approx 0.5 \chi^2 f_v^2 \frac{B_0^2}{\mu_0}
\]

(25)