

Field-Induced Layer Formation in Dipolar Nanofilms

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Using molecular dynamics simulations, we demonstrate that the layering of confined colloidal particles with dipolar interactions, such as ferrofluids, in slablike geometries can be controlled by homogeneous external fields. For suitable surface separations, strong fields directed perpendicular to the film plane do not only align the particles but create additional layers in the system. The reverse effect occurs with an in-plane field which can induce a collapse of layers. Both effects are accompanied by pronounced particle rearrangements in lateral directions. Our simulation results are consistent with recent experiments of ferrofluids at surfaces.

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Colloidal particles with dipolar interactions such as ferrofluids (nanosized permanent magnets in liquid carriers) and polarizable colloids (where dipole moments can be induced) are outstanding examples of soft materials whose structural and rheological properties can be controlled by external fields. Macroscopically, the possibility to position ferro-droplets by magnetic fields is used, e.g., in seals, loudspeakers, and in magnetic drug targeting [1]. On the nanoscale, magnetic fields combined with the directional character of the dipolar interactions induce aggregation of the particles into chains (see, e.g., [2]) and highly ordered clusters [3], yielding a dramatic increase of the viscosity [4] and thermal conductivity [5] of ferrofluids. Similar aggregation effects occur in other dipolar colloids [6], and indeed, field-driven self-assembly into predefined microstructures is now considered a promising route to design novel materials [6–8]. Also, external fields can trigger phase transformations, examples being the magnetic field-induced crystallization of superparamagnetic colloids [9,10] and corresponding binary mixtures [11], and the electric field-induced solid-solid transitions [12,13] in polarizable systems.

The present Letter deals with the *combined* effect of external fields and fluid-wall forces occurring in dipolar suspensions close to surfaces. It is well known that surfaces alone (irrespective of the nature of the interparticle forces) can induce a *layering* of the particles [14] in the direction normal to the surfaces. Indeed, layering of ferrofluids [15,16] and paramagnetic colloids [17] has been observed experimentally and in computer simulations of related model systems [18,19]. This prompts the question of how the layering could be manipulated by external magnetic (or electric) fields, a topic which might become particularly relevant for a controlled growth of magnetically nanostructured interfaces, including potential applications for data storage. Indeed, in a recent neutron-reflectometry study [16] of dispersed Fe₃O₄ nanoparticles at a SiO₂ surface, it was demonstrated that magnetic fields directed perpen-

dicular to the surface induce *smectic-like* ordering, whereas fields parallel to the interface strongly disturb the layering [16]. However, a precise understanding of the interplay between dipolar and surface forces is still missing.

In the present Letter, we report results from Molecular Dynamics (MD) computer simulations of a simple dipolar model fluid subject to two plane-parallel surfaces plus external magnetic (or electric) fields directed parallel or perpendicular to the surfaces. Considering a variety of surface separations and field strengths, and several thermodynamic states, we demonstrate that the experimentally observed field-induced effects [16] are indeed a generic phenomenon which can be explained by our minimal, dipole-dominated model. Further, we show that the layering effects in nanoconfined systems can be inferred from the solvation force accessible in surface-force experiments (see, e.g., [20]).

Our model fluid consists of spherical particles of diameter σ with embedded point dipole moments $\boldsymbol{\mu}_i$, $i = 1, \dots, N$. The total (“Stockmayer”) interaction between two particles with distance $r = |\mathbf{r}|$ consists of a (truncated and shifted) Lennard-Jones (LJ) potential, $u_{\text{LJ}}(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, and the long-range, anisotropic dipole-dipole potential given as $u_{\text{DD}}(12) = r^{-3}[\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - 3(\boldsymbol{\mu}_1 \cdot \mathbf{r})(\boldsymbol{\mu}_2 \cdot \mathbf{r})/r^2]$. The reduced temperature is set to $T^* = k_B T / \epsilon = 1.35$ (with k_B and T being Boltzmann’s constant and true temperature, respectively) and the reduced dipole moment $m^* = \mu / \sqrt{\epsilon \sigma^3} = 2.0$, corresponding to a system with dominant dipolar interactions (indeed, switching off the LJ attraction does not significantly change our results). The resulting dipolar coupling parameter $\lambda = \mu^2 / k_B T \sigma^3 \approx 2.96$ is in the range considered in recent ferrofluid experiments [3]. Spatial confinement of the particles is modeled by two plane-parallel, smooth walls located at $z = \pm L_z/2$ and of infinite extent in the x - y plane. We employ a “9-3” fluid-wall potential including repulsive and attractive contributions [21]. The con-

finned fluids are subject to a homogeneous magnetic field \mathbf{H} directed either perpendicular to the surfaces, i.e., $\mathbf{H} = \mathbf{H}_z$, or in-plane, that is, $\mathbf{H} = \mathbf{H}_\parallel$. We consider a range of fields strengths up to the (still realistic [3]) value $H^* = \mu H/k_B T \approx 100$. Most of the presented data correspond to a reduced density $\rho^* = \rho\sigma^3 = 0.6$ to have significant layering already at $H^* = 0$, but we have included various results at smaller and larger ρ^* . The calculations are performed using constant-temperature MD simulations with $N = 500$ particles, using a standard leap-frog algorithm [22] to solve the translational and rotational equations of motion (see [18] for details). Long-range interactions are taken into account via an Ewald summation suitable for a slab geometry [21,23], with conducting boundary conditions parallel to the surfaces and insulating ones in z -direction (the latter are not expected to influence the results qualitatively [24]). The simulations were started from zero-field configurations generated as described before [18]. Typical MD runs at $H^* > 0$ then consisted of about $7 - 8 \times 10^4$ time steps for equilibration and production.

A typical MD configuration at surface separation $L_z^* = L_z/\sigma = 5.0$ in zero field is shown in Fig. 1(a), illustrating two typical features of confined dipolar particles. First, the particles arrange into (four) layers as revealed even more directly by the oscillations in the corresponding number density profile $\rho(z)$ plotted in Fig. 2(a). Secondly, the particles close to the surfaces orient preferably along in-plane directions [see inset in Fig. 1(a)], thereby enhancing the possibility of energetically favorable head-to-tail arrangements.

Figure 1(b) shows the same system in a strong perpendicular field \mathbf{H}_z . We see that the field does not only orient the particles along \mathbf{H}_z but also strongly enhances the layering. In particular, as illustrated by the density profiles plotted in Fig. 2(a), a sufficiently strong field generates an *additional* (fifth) layer in the system.

What is the mechanism behind this layer formation? In Fig. 2(b), we present a typical in-plane correlation function $g_\parallel(R)$ illustrating the lateral structure in the contact layer (with $R^* = \sigma^{-1}\sqrt{\Delta x^2 + \Delta y^2}$), and two intralayer correlation functions $g_{\alpha\beta}^{\text{intra}}(R)$ reflecting the mutual arrangement

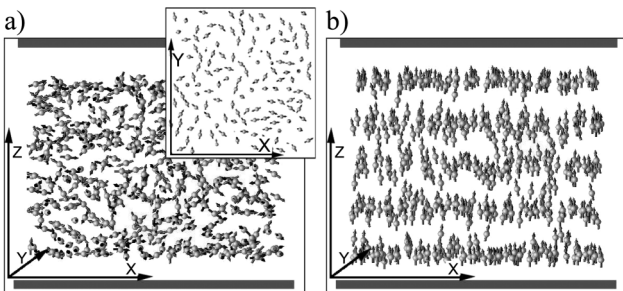


FIG. 1. Simulation snapshots at $L_z^* = 5$ (a) $H^* = 0$ (inset: top-view of the contact-layer), (b) $H_z^* = 74$.

of particles in neighboring layers α and $\beta \neq \alpha$. As seen from $g_\parallel(R)$ (top), a strong perpendicular field shifts the first peak from $R^* \approx 1$ (zero field) to $R^* \approx 1.2$, indicating a significant increase of the nearest-neighbor distance *within* the layer. This is reasonable since the field-induced alignment of the dipole moments in side-by-side configurations induces repulsive interactions and is thus energetically unfavorable. At the same time, the main peak of the correlation function $g_{12}^{\text{intra}}(R)$ (middle) moves from $R^* \approx 0.9$ ($H^* = 0$) to $R^* \approx 0.7$ ($H_z^* = 74$). Thus, looking from a particle in layer 1 (contact layer), its nearest neighbor in the adjacent layer 2 is “pulled” into the range of lateral separations where the interaction between two aligned, yet vertically displaced dipoles becomes attractive. Indeed, from a purely energetic point of view, one might rather expect *perfect* head-to-tail configurations in vertical directions [i.e., a main peak of $g_{12}^{\text{intra}}(R)$ at $R^* \approx 0$]. We do not see this behavior at $\rho^* = 0.6$ because the layer spacing in field is markedly smaller than the sphere diameter (in fact, such head-tail configurations do occur at lower densities). Finally, particles in the next-nearest layer 3 sit on top of those in layer 1 as revealed by the peak at $R^* \approx 0$ in $g_{13}^{\text{intra}}(R)$ [bottom of Fig. 2(b)]. Given the structural rearrangements in lateral directions, we conclude that the new layer generated by \mathbf{H}_z allows us, at the same time, to increase the in-plane distance between neighboring particles and to support attractive configurations of particles in different layers.

Clearly, a prerequisite for the lateral rearrangements is the field-induced alignment of the particles. Thus, the layer formation strongly depends on the field strength: If \mathbf{H}_z is too small, it cannot orient the particles against their preferred in-plane orientation in zero field [see inset in Fig. 1(a)] and against the macroscopic, density-dependent

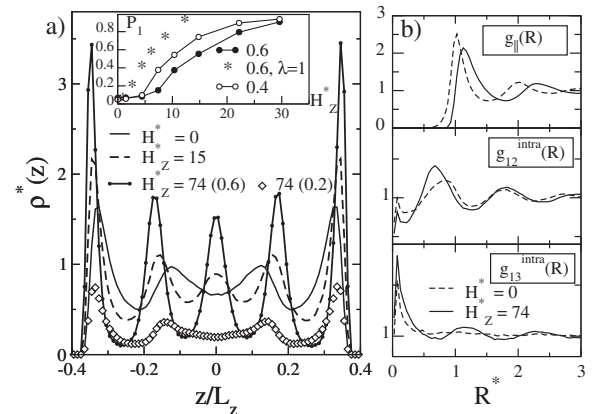


FIG. 2. (a) Density profiles at $L_z^* = 5.0$ and $\rho^* = 0.6$ (in \mathbf{H}_z). Included is a profile at $\rho^* = 0.2$ and $H_z^* = 74$ (bottom curve). Inset: Magnetization as function of H_z^* at $\rho^* = 0.6$, $\rho^* = 0.4$, and $\rho^* = 0.6$ with $\lambda = 1$ (see labels). (b) Inter- and intra-layer correlation functions ($\rho^* = 0.6$) at zero field and at $H_z^* = 74$ yielding five layers 1–5. Top: in-plane (contact layer, 1), middle: intra-layer (1 + 2), bottom: intra-layer (1 + 3).

demagnetizing field which weakens the impact of \mathbf{H}_z (irrespective of the boundary conditions [24]). The competition between field and surface effects becomes also manifest in the magnetization order parameter $P_1 = N^{-1}|\langle\sum_{i=1}^N \mu_{i,z}\rangle|$ [22] plotted in the inset of Fig. 2(a). Significant ordering occurs only for $H_z^* \gtrsim 15$, and indeed, only above this strength, the field is able to create a new layer. Clearly, this threshold value depends on the thermodynamic state considered. In systems with lower density or smaller dipolar coupling λ , the surface-induced in-plane ordering is less pronounced, such that the value H_z^* required for significant magnetization and accompanying layer creation decreases as well. This is reflected by the corresponding functions $P_1(H_z^*)$ [see inset of Fig. 2(a)]. An implicit consequence of our results is that, at fixed H_z^* , the number of layers can also be changed by varying ρ^* . For example, at $H_z^* = 74$ and $L_z^* = 5.0$, we observe five layers at $\rho^* = 0.6$ but only four at $\rho^* = 0.2$ [see Fig. 2(a)]. This is consistent with experiments of *compression*-induced layering transitions in confined paramagnetic colloids [17].

Of course, in the relatively dense, nanoconfined systems considered here, field-induced formation of new layers is not possible at *arbitrary* surface separations. A convenient indicator of the layering effects is the normal pressure, $P_z = -A^{-1}\partial\mathcal{F}/\partial L_z$ [21] (with \mathcal{F} and A being the free energy and the lateral area), as a function of L_z^* . This function is directly related to the solvation force measurable in surface-force experiments [20]. The corresponding zero-field result at $\rho^* = 0.6$ is plotted in Fig. 3(a) for a small range of separations allowing the system to form three ($L_z^* \lesssim 4.2$) to four layers ($L_z^* \gtrsim 4.3$). The transition between these regimes is indicated by oscillations in $P_z^*(L_z^*)$, which are typical of confined fluids [21]. An analysis of the corresponding profiles $\rho^*(z)$ reveals that \mathbf{H}_z can create a new layer only for separations in the vicinity of the *minima* of $P_z^*(L_z^*)$ (at $H^* = 0$). This is in a

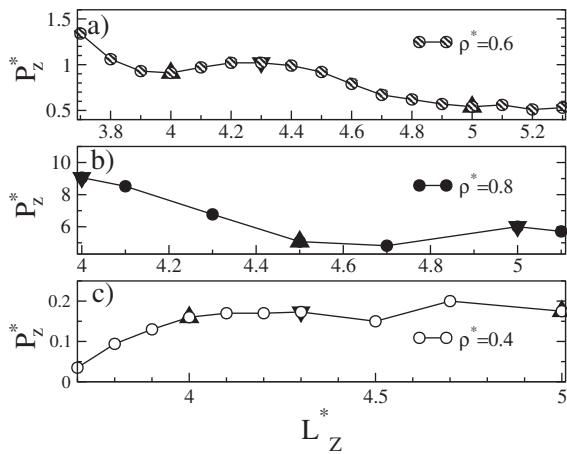


FIG. 3. (a)–(c) Zero-field normal pressure as function of L_z^* at three densities. The triangles up (down) indicate where \mathbf{H}_z (\mathbf{H}_{\parallel}) can create (destroy) a layer.

way expected since the minimum reflects a “comfortable” arrangement of the confined particles, which allows for some compression in vertical direction. For other separations, particularly at the maximum of P_z^* in Fig. 3(a), a perpendicular field leads only to a sharpening of $\rho^*(z)$. The same correlation between the minima in $P_z^*(L_z^*)$ and field-induced layer creation is found at the higher density $\rho^* = 0.8$ [see Fig. 3(b)]. On the other hand, upon decrease of ρ^* , the zero-field layering becomes less pronounced as reflected by the softer shape of $P_z^*(L_z^*)$ [see Fig. 3(c)]. In such systems, a perpendicular field can thus create new layers in broader range of surface separations.

Completely different layering effects occur with in-plane fields, \mathbf{H}_{\parallel} . Because of the preferred in-plane orientation of the dipoles already at $H^* = 0$ [see Fig. 1(a)], it is clear that \mathbf{H}_{\parallel} can align the dipoles much more easily than a perpendicular one (also note that in-plane ordering does not induce a macroscopic demagnetization field). A surprising effect is that an in-plane field can also *destroy* zero-field layers. Consider a surface separation for which the zero-field normal pressure is in a *maximum*, such as $L_z^* = 4.3$ ($\rho^* = 0.6$) or $L_z^* = 5.0$ ($\rho^* = 0.8$) [see Figs. 3(a) and 3(b)]. Under such conditions, \mathbf{H}_{\parallel} not only softens the oscillations in the density profiles compared to $H^* = 0$, it also decreases the number of layers by one [see Figs. 4(a) and 4(b)]. Typical in-plane particle configurations at $\rho^* = 0.6$ and 0.8 and $H_{\parallel}^* > 0$ are shown in Fig. 4(c). As expected from the behavior of two-dimensional dipolar fluids [25], the field \mathbf{H}_{\parallel} leads to formation of aligned, chainlike aggregates of the particles with head-to-tail orientations of the dipole moments. Moreover, as seen particularly at the higher density ($\rho^* = 0.8$), neighboring chains tend to be shifted relative to one another, resembling locally a hexagonal structure. Indeed, field-induced local hexagonal ordering has also been observed in recent experiments [3]. In the z -direction, on the other hand, the chains rather *repel* each other due to the lack of pronounced vertical correlations [26]. This mutual disturbance might explain

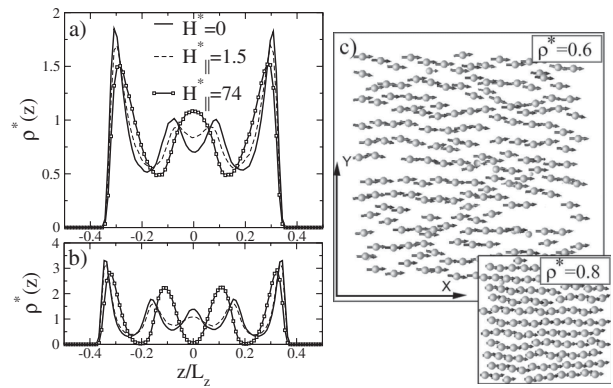


FIG. 4. (a) Density profiles at $\rho^* = 0.6$ and $L_z^* = 4.3$ (parallel field). (b) Same for $\rho^* = 0.8$ and $L_z^* = 5.0$. (c) Snapshots of the contact layers at the two densities and $H_{\parallel}^* = 74$.

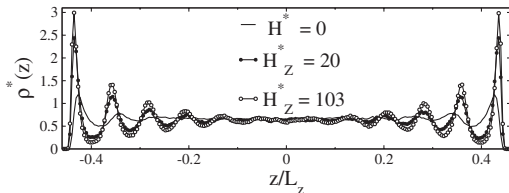


FIG. 5. Density profiles at $L_z^* = 12$ (perpendicular field).

the destruction of a layer and expansion of the remaining ones [see Fig. 4(a) and 4(b)].

The strong impact of external fields on the layering is not restricted to the nanoscopic confined systems discussed so far. In Fig. 5, we consider density profiles of a *mesoscopic* system, where L_z^* is so large that the inner region in zero field is bulklike (i.e., homogeneous density). Thus, we are essentially looking at two *decoupled* dipolar fluids each being influenced by one confining surface. Switching on a perpendicular field, which is sufficiently strong to overcome the surface-induced in-plane ordering ($H_z^* \gtrsim 10$), the amplitude of oscillations in $\rho^*(z)$ and the resulting number of layers close to each surface strongly increases. At the same time, the layer separation decreases. These features are fully consistent with the smectic-like ordering seen in the neutron-reflectometry experiments of ferrofluids at a SiO_2 surface [16].

To summarize, we have shown via computer simulations that the surface-initiated layering of dipolar particles, particularly the number of layers and their internal structure, can be controlled by external fields. Most spectacularly, the field can create or destroy layers depending on its direction relative to the surface(s), in agreement with recent experiments of ferrofluids [16]. For nanoconfined (and sufficiently dense) systems, these effects can be inferred from solvation force experiments. The similarity of our results at several thermodynamic states indicates that the field-induced layering effects are a rather generic feature of confined dipolar liquids.

An interesting question concerns the relation between the field-induced layering effects reported here and the field-induced formation of solid mesostructures (labyrinths, cylinders) [27,28] in dilute solutions of cobalt nanocrystals evaporated at interfaces. We suspect that the absence of such patterns in our study is mainly due to the liquidlike densities considered. For even higher densities, one could imagine field-induced crystallization [9] resulting in different 3D solidlike structures [12]. A more detailed study of these topics is under way.

Finally, given that we observe the most interesting effects when H^* is larger than the dipolar coupling parameter λ , we expect our findings to be transferable to colloidal

systems of *induced* dipoles such as polarizable or paramagnetic particles. Our results therefore contribute to the general understanding of dipolar colloids as building blocks for novel micro- and nanostructures such as storage media and optical devices [6,12].

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- [1] R. Jurgons *et al.*, J. Phys. Condens. Matter **18**, S2893 (2006).
 - [2] W.-X. Fang *et al.*, Europhys. Lett. **77**, 68004 (2007).
 - [3] M. Klokkenburg *et al.*, Phys. Rev. Lett. **97**, 185702 (2006).
 - [4] S. Odenbach, Int. J. Mod. Phys. B **14**, 1615 (2000).
 - [5] J. Philip *et al.*, Appl. Phys. Lett. **91**, 203108 (2007).
 - [6] O.D. Velev and K.H. Bhatt, Soft Matter **2**, 738 (2006).
 - [7] X. Zhang *et al.*, J. Phys. Chem. C **111**, 4132 (2007).
 - [8] S.C. Glotzer and M.J. Salomon, Nat. Mater. **6**, 557 (2007).
 - [9] K. Zahn *et al.*, Phys. Rev. Lett. **82**, 2721 (1999).
 - [10] L.E. Helseth *et al.*, Langmuir **21**, 7518 (2005).
 - [11] J. Fornleitner *et al.*, Soft Matter **4**, 480 (2008).
 - [12] A. Yethiraj *et al.* Phys. Rev. Lett. **92**, 058301 (2004).
 - [13] A.P. Hynninen and M. Dijkstra, Phys. Rev. Lett. **94**, 138303 (2005).
 - [14] J.N. Israelachvili and R.M. Pashley, Nature (London) **306**, 249 (1983).
 - [15] C.Y. Matuo *et al.*, Phys. Rev. E **56**, R1310 (1997).
 - [16] A. Vorobieff, J. Major, H. Dosch, G. Gordeev, and D. Orlova, Phys. Rev. Lett. **93**, 267203 (2004).
 - [17] L.E. Helseth *et al.*, Phys. Rev. E **71**, 062402 (2005).
 - [18] V.A. Froltsov and S.H.L. Klapp, J. Chem. Phys. **124**, 134701 (2006); **126**, 114703 (2007).
 - [19] V. Ballenegger and J.P. Hansen, J. Chem. Phys. **122**, 114711 (2005).
 - [20] S.H.L. Klapp, Y. Zeng, D. Qu, and R. von Klitzing, Phys. Rev. Lett. **100**, 118303 (2008).
 - [21] M. Schoen and S.H.L. Klapp, in *Rev. Comp. Chem.*, edited by K.B. Lipkowitz (John Wiley & Sons, New York, 2007), Vol. 24.
 - [22] M.P. Allen and D.J. Tildesley, *Computer Simulation of Liquids* (Academic, London, 1987).
 - [23] I.-C. Yeh and M.L. Berkowitz, J. Chem. Phys. **111**, 3155 (1999).
 - [24] S.H.L. Klapp, Mol. Simul. **32**, 609 (2006).
 - [25] J.-J. Weis, Mol. Phys. **103**, 7 (2005).
 - [26] Indeed, at even larger ρ^* , one could imagine three-dimensional chain structures resembling those observed in electrorheological fluids (see R. Tao and J.M. Sun, Phys. Rev. Lett. **67**, 398 (1991) and [12]).
 - [27] Y. Lalatonne *et al.*, Nat. Mater. **3**, 121 (2004).
 - [28] J. Legrand *et al.*, Adv. Mater. **13**, 58 (2001).