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Universal non-monotonic smectic fluctuations of liquid crystal films in a magnetic field

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Abstract. Free-standing liquid crystal films with positive diamagnetic susceptibility can have the smectic ordering enhanced by an external field applied perpendicular to the plane layers. Within a quadratic functional integral approach, we investigate the interplay between the smectic order induced by an external field H and that due to the surface tension γ between the film and the surrounding gas. We find that the average smectic fluctuation is a non-monotonic function of film thickness, with a characteristic thickness scale ξ_H delimiting the predominance of surface tension and magnetic field effects. This characteristic thickness obeys simple asymptotic power-law relations as a function of the ordering terms which allows us to represent the average smectic fluctuations in a universal scaling form.

PACS. 61.30.Hn Surface phenomena: alignment, anchoring, anchoring transitions, surface-induced layering, surface-induced ordering, wetting, prewetting transitions, and wetting transitions – 61.30.Gd Orientational order of liquid crystals; electric and magnetic field effects on order – 61.30.Dk Continuum models and theories of liquid crystal structure

1 Introduction

The rich phenomenology presented by the thermal properties of liquid crystals makes of them a class of very important physical systems, both from the experimental and theoretical point of views [1,2]. In particular, they may display a variety of phase transitions with quite distinct features such as second order phase transitions, thinning transitions as well as partial, complete and layer by layer wetting [3–7]. Liquid crystals provide, therefore, ideal model systems to test several predictions of phase transition and critical phenomena theories. The progress in the experimental ability to prepare free standing liquid crystal films has recently motivated further studies about the interplay between surface ordering fields and finite size effects.

Heat capacity measurements on free-standing smectic films observed a non-monotonic behavior of the bulk transition temperature between smectic-A and hexatic-B phases as a function of the film thickness l [8]. This unusual behavior was indeed explained theoretically as a result of the interplay between finite-size and surface ordering effects [9]. The presence of a surface ordering field introduces a characteristic thickness scale ξ_s and a universal function $F(l/\xi_s)$ governs the approach of the heat-capacity maximum to its thermodynamic limit. $F(l/\xi_s)$ decreases for $l/\xi_s \ll 1$ due to the predominance of surface ordering in thin films. On the other hand, finite size effects dominate for thick films and $F(l/\xi_s)$ increases for $l/\xi_s \gg 1$, in full agreement with the experimental results [8].

Usually, the main surface ordering field in free-standing smectic films is represented by a surface tension which strongly reduces fluctuations in the smectic order and provides the characteristic quasi-long range order with logarithmically diverging fluctuations [10,11]. The surface tension strength determines the overall profile of smectic fluctuations, whose average has a monotonic behavior as a function of film thickness [11,12]. In the hexatic-B phase, a universal non-monotonic finite-size scaling of the mean angle fluctuations was predicted for films with enhanced surface couplings [13]. Similarly, non-monotonic angle fluctuations also results from the presence of a small surface hexatic ordering field [13] which can be induced by a weak tilt of the surface molecules [14].

Recently, there have been many investigations on the effects caused by an external magnetic field in the thermal properties of liquid crystals. It is known that the magnetic field induces alignment of the director, both in nematic and smectic phases [15–17]. Also, the influence of an applied magnetic field on the critical behavior of liquid crystals have been extensively investigated [18–21]. In smectic films, the magnetic field couples with the layer displacement in such a way that it can enhance or degrade the smectic order depending on the specific diamagnetic anisotropy and field direction. In films with

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negative diamagnetic anisotropy under a magnetic field applied perpendicularly to the layer plane, the smectic order is degraded by the magnetic field, an effect similar to the Helfrich's effect which can occurs in infinite samples of cholesteric liquid crystals [22,23]. A decrease of the smectic order can also be observed in films with positive diamagnetic anisotropy when the external field is parallel to the layer plane. In contrast, enhanced order can be established in films with negative (positive) diamagnetic anisotropy under parallel (perpendicular) magnetic fields.

In this work, we will examine in detail the effects of an ordering magnetic field in the smectic fluctuations of free-standing films. Here, we consider films with positive anisotropy χ_a under a perpendicular magnetic field. Using a Gaussian functional integral approach, we will study the interplay between the enhancing of the smectic order induced by surface tension and external magnetic field. Field ordering is expected to become more relevant for thick films as it couples with all layers. By computing the average smectic fluctuations, we are going to identify and characterize the scaling behavior of the typical thickness delimiting the crossover between surface tension and magnetic field predominance on the smectic ordering. Within such scaling analysis, the smectic fluctuations can be represented in a universal form as a function of the normalized thickness.

2 Free energy and smectic fluctuations

Free standing smectic-A films can be described as stacked two-dimensional liquid layers surrounded by gas. The small displacement of the ith smectic layer from its original equilibrium position $z = id$ in the point $\mathbf{r}$ is represent by $u_i(\mathbf{r})$, where d is the average layer spacing. Within an harmonic approximation, the Hamiltonian for a thin smectic-A film with N layers is given by [11]

$$\mathcal{H} = \int_a^L \mathrm{d}^2 r \left[\sum_{i=1}^{N} \frac{dK}{2} [\triangle u_i(\mathbf{r})]^2 + \sum_{i=1}^{N-1} \frac{B}{2d} [u_{i+1}(\mathbf{r}) - u_i(\mathbf{r})]^2 + \frac{\gamma}{2} |\nabla u_1(\mathbf{r})|^2 + \frac{\gamma}{2} |\nabla u_N(\mathbf{r})|^2 \right]. \quad (1)$$

Here L is the transverse size of the film and a is a cutoff length of the order of the molecular diameter. γ is the surface tension that acts in surface layers representing the effective interaction between the surrounding gas and the smectic-A film. This surface tension tends to reduce deformations at the surface of the films penalizing any gradient of the surface layer displacement, with the equilibrium direction being defined by the film holders used in the free standing technique [24]. K is the elastic constant associated with layer undulations and B is the elastic coupling between neighboring layers. Both K and B depend considerably of the layer index i at temperatures close to the nematic-smectic transition temperature [25]. However, as the smectic order is stabilized, these elastic couplings become uniform along the whole film, except near the surface layers [25]. The effects of stronger surface constants in the smectic order of free standing films were already investigated in detail [12] and will not be explored in the present work.

Each smectic-A layer consists of long molecules that in average are aligned perpendicularly to the layer plane. The average local molecular alignment can be represented by a unit vector $\mathbf{n}$. Thermal fluctuations deviate the molecular alignment from this prefered direction, which also contributes to increase the fluctuations in the smectic order. The presence of an external magnetic field H applied perpendicularly to the layer plane forces the molecular alignment to keep itself along or perpendicular to this direction, depending on the diamagnetic anisotropy of the molecules. As a result, one can have either an increase or a decrease of the smectic order induced by the external magnetic field. Specifically, the field induced alignment results in a net magnetization M in the form [1]

$$\mathbf{M} = \chi_\perp \mathbf{H} + (\chi_\parallel - \chi_\perp)\mathbf{H}, \quad (2)$$

where $\chi_\perp$ and $\chi_\parallel$ are the diamagnetic susceptibilities perpendicular and parallel to the director, respectively. The difference between $\chi_\perp$ and $\chi_\parallel$ is named diamagnetic anisotropy χ_a. Both $\chi_\perp$ and $\chi_\parallel$ are negative but χ_a is in general positive. From equation (2), one can derive the additional free-energy associated with the presence of an external magnetic field as

$$\mathcal{H}_M = \int_a^L \mathrm{d}^2 r \left[\sum_{i=1}^{N} \frac{d\chi_a H^2}{2} |\nabla u_i(\mathbf{r})|^2 \right]. \quad (3)$$

Here we can observe that for $\chi_a > 0$, the presence of a perpendicular magnetic field increases the smectic order. The resulting Hamiltonian that describes the displacement fluctuations of free standing smectic-A films in the presence of such magnetic field is given by

$$\mathcal{H}_T = \mathcal{H} + \mathcal{H}_M. \quad (4)$$

Employing a continuous Fourier transform with respect to $\mathbf{r}$, the above quadratic Hamiltonian can be partially diagonalized, thus providing simple expressions for some thermodynamic quantities of interest. In particular, it's straightforward to show that the average smectic fluctuation of the ith layer is given by

$$\langle u_i^2 \rangle = d^2 \frac{k_B T}{a^2 \gamma_c} \int_{\frac{2\pi a}{L}}^{2\pi} \frac{\mathrm{d}^2 q}{(2\pi)^2} \left(M^{-1} \right)_{i,i}, \quad (5)$$

where q is the wave-vector of layer ondulations measured in units of the inverse microscopic cutoff length $1/a$. $\sigma_i = \sqrt{\langle u_i^2 \rangle}$ is the root mean square displacement of layer i. The only nonzero elements of the interaction matrix $\mathbf{M}$

are

$$M_{1,1} = M_{N,N} = \left(\frac{d}{a}\right)^2 \left[\left(\frac{\gamma}{\gamma_c}\right) + \left(\frac{H}{H_c}\right)^2 \left(\frac{d}{a}\right)\right] q^2 + \left(\frac{\lambda_c}{a}\right)\left(\frac{d}{a}\right)^3 q^4 + \left(\frac{d}{a}\right)\left(\frac{a}{\lambda_c}\right) \quad (6)$$

$$M_{i,i} = \left(\frac{H}{H_c}\right)^2 \left(\frac{d}{a}\right)^3 q^2 + \left(\frac{\lambda_c}{a}\right)\left(\frac{d}{a}\right)^3 q^4 + \left(\frac{d}{a}\right)\left(\frac{a}{\lambda_c}\right), \quad i = 1, N-1 \quad (7)$$

$$M_{i,i+1} = M_{i+1,i} = -\left(\frac{d}{a}\right)\left(\frac{a}{\lambda_c}\right), \quad i = 1, N-1 \quad (8)$$

where we represented all contributions in form of dimensionless terms. $\lambda_c = \sqrt{K/B}$ is a characteristic length scale and $\gamma_c = \sqrt{KB}$ is a characteristic surface tension. Here, we also introduced a characteristic magnetic field $H_c = \sqrt{\gamma_c / a\chi_a}$.

In the absence of an external magnetic field, a detailed analysis of the influence of the surface tension on the profile of smectic fluctuations was already employed [11,12]. For the regime of surface tensions larger than the characteristic tension γ_c, the smectic fluctuations profile has a negative concavity, reflecting the strong surface anchoring which enhance the smectic order of the surface layers as compared to the bulk ones [11]. For the regime where the surface tension is weaker than the characteristic tension, the fluctuation profile presents a positive concavity [12]. In this case, the ordering induced by the surface anchoring is not strong enough to overcome the enhanced fluctuations near the open surfaces. In the next section, we will investigate the interplay between surface and bulk ordering of free-standing films in the presence of a magnetic field. In particular, we will employ a scaling analysis of the competing effects of strong surface tension and magnetically induced order as a function of the film thickness.

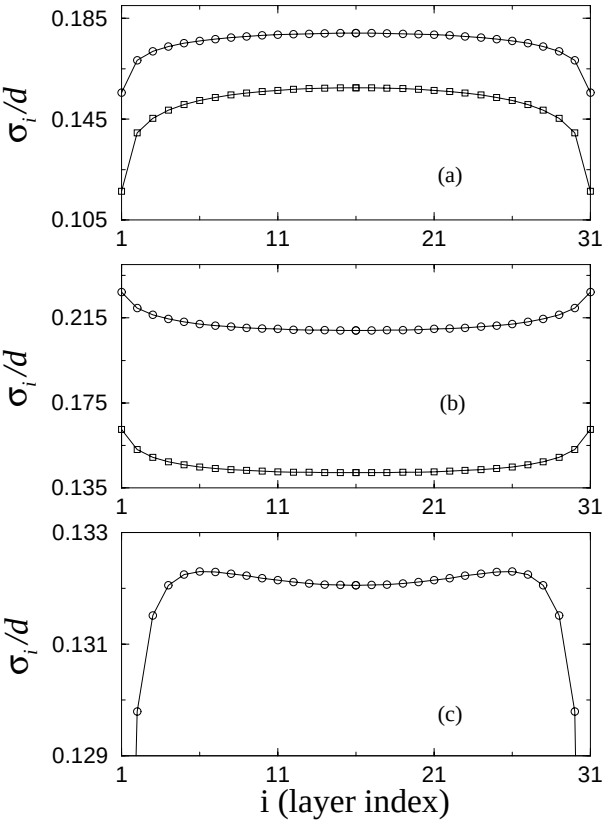

Fig. 1. Profile of smectic fluctuations for a 31-layers film. We use experimentally typical values $K = 1 \times 10^{-6}$ dyn and $B = 2.5 \times 10^7$ dyn/cm^2 for films with a positive diamagnetic anisotropy $\chi_a = 10^{-7}$. The values for the magnetic field and surface tension are (a) $H = 0$, $\gamma = 3\gamma_c$ (circles) and $\gamma = 6\gamma_c$ (squares); (b) $H = 2H_0$ (circles), $H = 3H_0$ (squares) and $\gamma = 0$; (c) $H = 3H_0$ and $\gamma = 3\gamma_c$, where we used as a reference magnetic field $H_0 = 0.07H_c$. Notice that the smectic fluctuations have a non-monotonic behavior under action of both strong anchoring $\gamma > \gamma_c$ and external magnetic field.

3 Surface tension and magnetic field ordering: scaling analysis

In Figure 1, we show our main results for the profile of smectic fluctuations on a 31-layers film through numerical integration of equation (5). We used typical values for elastic constants $K = 1 \times 10^{-6}$ dyn and $B = 2.5 \times 10^7$ dyn/cm^2. Further, we considered $d = 30$ Å, $a = 4$ Å, $\chi_a = 10^{-7}$, $L = 1$ cm, $k_BT = 4 \times 10^{-14}$ erg. In Figure 1a, we have the profile of smectic fluctuations for free-standing film under the action of a strong surface tension in the absence of an external magnetic field. The profile has a negative concavity [11], with the surface tension favoring surface ordering. The fact that, under strong anchoring, fluctuations are larger at bulk layers is responsible for the layer thinning transitions observed to occur in smectic films [4]. For films with free boundaries, a magnetic field applied perpendicularly to the layer plane couples with all layers displacement thus directly reducing fluctuations in the whole film. However, as the surface layers are free, they fluctuate more than bulk layers resulting in a profile with positive concavity, as shown in Figure 1b. In free-standing films strongly anchored by a surface tension and under an external magnetic field the profile of smectic fluctuations displays a crossover between the above two regimes of negative and positive concavities. Figure 1c shows this crossover, where the profile presents a non-monotonic behavior as a function of the layer index i. This non-monotonicity is caused by the fact that, while the magnetic field couples with all layers, surface tension couples just with the external layers of film and its effect become less important in inner layers. It is worth to notice that the existence of an inflexion point in the profile of smectic fluctuations caused by mixed boundary conditions, was correlated with the emergence of repulsive fluctuation-induced interactions between the surface layers [12]. The above reported non-monotonic profile may imply in a non-trivial thickness dependence of the nature

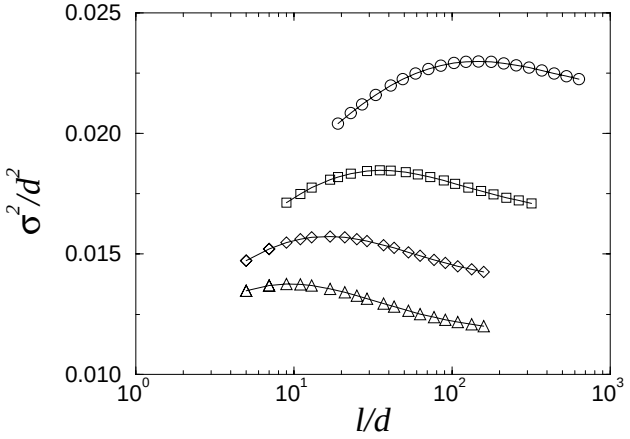

Fig. 2. Mean square layer displacement σ^2 of smectic films *versus* normalized thickness l/d. Coupling constants and diamagnetic anisotropy are the same as in Figure 1 and the surface tension was made $\gamma = 6\gamma_c$. The values for magnetic fields are $H = H_0$ (circles), $H = 2H_0$ (squares), $H = 3H_0$ (diamonds) and $H = 4H_0$ (triangles). In all cases, the mean square layer displacement has a non-monotonic dependence on the film thickness. It exhibits a maximum at a characteristic thickness ξ_H, which is a function of surface tension and external magnetic field.

of the Casimir-like interaction in smectic free-standing films under an external magnetic field.

This non-monotonic behavior of the smectic fluctuations profile indicates the existence of distinct thickness regimes where surface tension and magnetic field act as the dominant ordering term. To investigate this interplay between magnetic field and surface tension ordering, we compute the average squared layer displacement given by

$$\sigma^2 = \frac{1}{N}\sum_{i=1}^{N}\sigma_i^2. \tag{9}$$

We plot σ^2 as a function of the film thickness l for several magnetic fields and the same surface tension, as shown in Figure 2. It can be noticed that σ^2 has a non-monotonic dependence with film thickness, achieving a maximum at a characteristic thickness ξ_H. For small l, the average layer displacement grows with film thickness, once surface ordering is more relevant than the bulk one. On the other hand, σ^2 decreases with increasing film thickness for large l. This trend is due to the fact that in thick films the surface ordering is not efficiently transmitted to the inner layers. In contrast, the growth in bulk smectic order imposed by the external magnetic field reduces global fluctuations. The interplay of the above two trends results in the existence of the above mentioned characteristic film thickness for which the average smectic fluctuations are maximum. Both ξ_H and the maximum fluctuation $\sigma^2_{\max}$ depend on the magnetic field and surface tension. In the regime of strong anchoring, $\gamma > \gamma_c$, we verified that ξ_H increases with γ according to a power law $\xi_H \propto \gamma^2$ when the magnetic field is kept constant, as shown in Figure 3a.

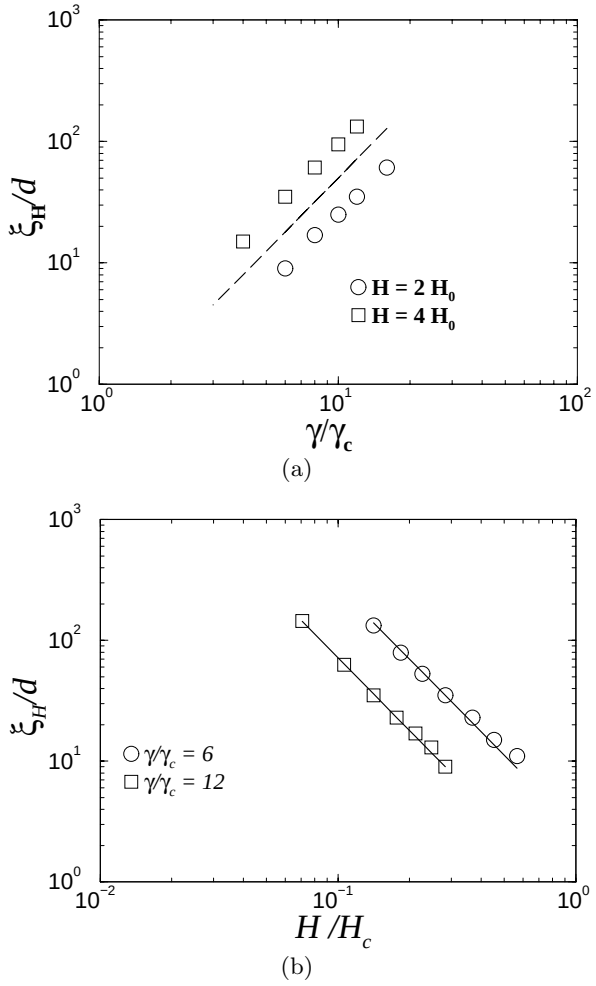

Fig. 3. (a) Characteristic thickness ξ_H/d *versus* surface tension and distinct magnetic fields. Coupling constants and diamagnetic anisotropy are the same as in Figure 1. For strong anchoring the characteristic thickness increases with the surface tension according to a power law $\xi_H \propto \gamma^2$. (b) Characteristic thickness ξ_H/d *versus* magnetic field for distinct surface tensions. The characteristic thickness decays with magnetic field according to a power law $\xi_H \propto H^{-2}$.

On the other hand, analysing the dependence of ξ_H on the magnetic field for fixed surface tension, we obtained that ξ_H decays according to a power law $\xi_H \propto \left(\frac{1}{H}\right)^2$, as shown in Figure 3b. Therefore, the thickness for which the smectic fluctuations are maximum scales as

$$\xi_H \propto \left(\frac{\gamma}{H}\right)^2. \tag{10}$$

The $\sigma^2_{\max}$ dependence on the surface tension for a fixed magnetic field is presented in Figure 4a. $\sigma^2_{\max}$ decreases with increasing surface tension, saturating at a finite value in the limit of very strong anchoring. However, as a function of the external magnetic field, $\sigma^2_{\max}$ presents a logarithmic decay, as shown in Figure 4b. The existence of simple scaling relations for both characteristic thickness and

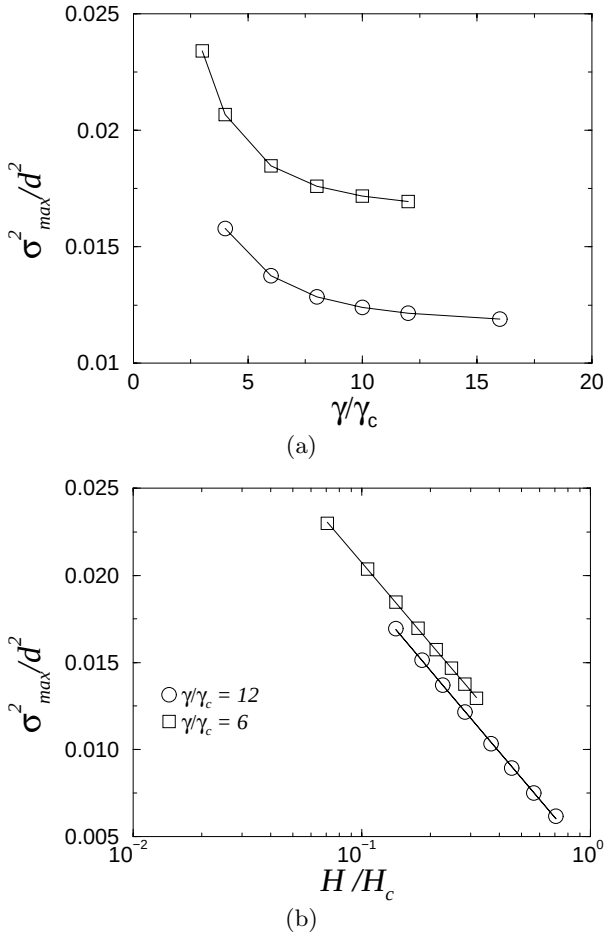

Fig. 4. (a) The maximum average squared smectic fluctuation $\sigma^2_{\max}$ *versus* surface tension for distinct magnetic fields. The values for magnetic fields are $H = 2H_0$ (squares) and $H = 4H_0$ (circles). For $\gamma \gg \gamma_c$ the maximum fluctuation converges to a constant value which depends of the applied magnetic field. (b) $\sigma^2_{\max}$ *versus* magnetic field for distinct surface tensions. The maximum fluctuation decays logarithmically with increasing magnetic field.

maximum average squared displacement, indicates that a universal scaling function governs the overall behavior of σ^2 as a function of l/ξ_H. In Figure 5, we employed a collapse of data from distinct values of the magnetic field (same data shown in Fig. 2). The resulting finite thickness scaling relation assumes the universal form

$$\frac{\sigma^2}{\sigma^2_{\max}} - 1 = \left(\frac{H}{H_c}\right)^{\frac{1}{2}} F\left(\frac{l}{\xi_H}\right). \qquad (11)$$

The asymptotic regime $l \ll \xi_H$ is achieved for very small magnetic fields. The surface ordering dominates this regime and smectic fluctuations grow with increasing film thickness. Otherwise, the asymptotic regime of $l \gg \xi_H$ sets up for strong magnetic fields with smectic fluctuations decreasing with film thickness but saturating at a finite value as $l/\xi_H \to \infty$.

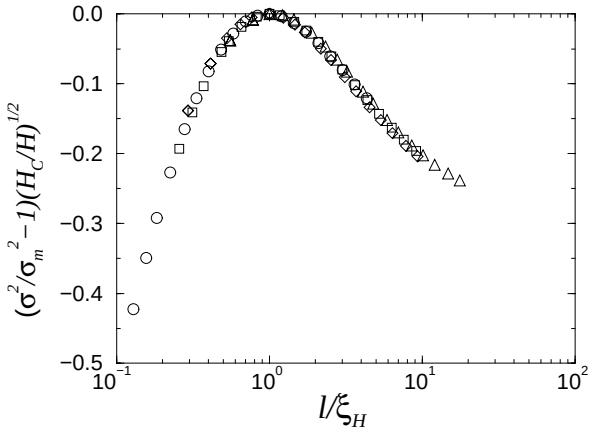

Fig. 5. Collapse of data from several values of magnetic field (same data of Fig. 2). The characteristic thickness ξ_H delimits the regions of predominance of surface induced ordering ($l \ll \xi_H$) and magnetic field induced ordering ($l \gg \xi_H$).

4 Summary and conclusions

In this work, we investigated theoretically the influence of an external magnetic field in the smectic fluctuations of thin free-standing liquid crystal films. We concentrated our attention to the case of an ordering magnetic field applied perpendicularly to the layers of a liquid crystal film with positive diamagnetic anisotropy. In the framework of a quadratic functional approach for the Hamiltonian, an exact expression for the fluctuation profile allowed for a detailed investigation of the interplay between the ordering effects of surface tension γ and magnetic field H. Finite-size scaling behavior of the average smectic fluctuations was found to be determined by a thickness scale $\xi_H \propto (\gamma/H)^2$. In the thin film regime of $l < \xi_H$ the surface tension ordering dominates and smectic fluctuations grow as the film thickness is increased. However, in the thick film regime of $l > \xi_H$ the surface ordering does not propagate efficiently to the inner layers and magnetic field ordering dominates. In this regime the average smectic fluctuations decreases with increasing thickness as the magnetic field couples with all layers and enhances the smectic order. As a result of the interplay between these two regimes, the average smectic fluctuation exhibits a maximum at the characteristic thickness ξ_H reflecting the non-monotonic nature of the fluctuations profile. Further, we found that the crossover between these regimes can be represented in a scaling form and reported on the relevant scaling exponents characterizing this universal behavior. Similar universal non-monotonic fluctuations are expected to take place in liquid crystal films under the influence of an electric field perpendicular to the plane layers [1,18,26]. The present results contribute with further understanding of the role played by external fields which may change the order of the nematic-smectic-A transition in liquid crystal films [19,20].

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