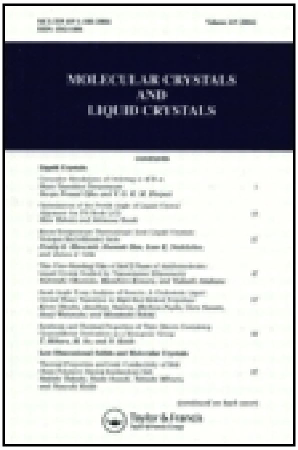

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Casimir Interactions and Instability of Thin Nematic Films

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Casimir Interactions and Instability of Thin Nematic Films

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We review our theoretical studies of mean-field and fluctuation-induced forces together with van der Waals force in a thin hybrid nematic film. We focus on the stability of nematic films frustrated by competing surface fields. Depending on temperature, anchoring strengths, and frustration, the films can be either stable, or they dewet the substrate through spinodal dewetting.

Keywords: confined liquid crystals; mean-field forces; pseudo-Casimir forces; stability of films; spinodal dewetting

INTRODUCTION

Liquid crystals confined on submicron scale exhibit a variety of interesting phenomena and are of great importance for electro-optical applications. Because of the high surface-to-volume ratio the effects of the confining surfaces are very important, although this does not necessarily imply a strongly deformed order parameter.[1,2] However, even a weak distortion of the ordering can result in a rather strong force induced by the liquid crystal because in this regime the fluctuation-mediated contribution to the force can be strongly amplified.[3]

In this paper we give a brief review of our recent studies of structural and van der Waals forces in microconfined systems with hybrid anchoring conditions.[2,4,5] Using Landau–de Gennes approach and techniques developed in our previous studies[2,4] we estimate the mean-field and fluctuation-mediated (pseudo-Casimir) forces as well as the van der Waals force for thin films with frustrating hybrid boundary conditions. We show that the stability of such films depends on the delicate details of surface properties, and we find that the recently observed dewetting of a thin 5CB film on a silicon wafer can be understood in terms of competing van der Waals and Casimir forces.[6]. The effects of the substrate-induced layering are not discussed here, however, for a special case of a presmectic film they are addressed elsewhere.[7]

In the next Section the model system and theory of stability of thin films are described in short. Then we describe the three contributions to the interaction between the confining substrates: the van der Waals, mean-field and pseudo-Casimir forces. Finally, we discuss the stability conditions for thin nematic depositions frustrated by hybrid anchoring.

STABILITY OF THIN FILMS

Most microconfined liquid-crystalline systems are characterized by more or less curved internal geometry. The confining geometries all share a common feature: the curved boundary and/or the antagonistic boundary conditions result in frustration which leads to a variety of equilibrium structures controlled by either temperature or size of the system. Although the behavior of these systems can be very complex, the basic physics of the confinement-induced frustration can be modeled by the so-called hybrid nematic cell — a nematic liquid crystal film confined by two parallel substrates that induce uniaxial nematic ordering but are characterized by different wetting and anchoring properties [Fig. 1(a)]; often one easy axis is homeotropic (H) and the other is planar (P).

The force between the interfaces includes the van der Waals and the structural force. In planar geometry, the disjoining pressure (i.e., the force between the interfaces per unit area) is defined by

$$\Pi = \frac{\mathcal{F}}{S} = -\frac{1}{S}\left(\frac{\partial F}{\partial d}\right)_{V,S}, \tag{1}$$

where F is the sum of van der Waals interaction potential and the total free energy of the system in question, d is the separation between the substrates, and S is the substrate area. The total free energy includes the mean-field part and the free energy of fluctuations.

We focus on a system that corresponds to the experimental setup used in a recent study of dewetting[6]: the model geometry consists of a slab of nematic liquid crystal on a solid substrate; the upper interface is free. Dynamically, the air-liquid crystal interface is not flat but wrinkled due to capillary waves. Because the disjoining pressure is different for different thicknesses which are caused by capillary waves the film may be unstable; the process of decomposition of such a film is known as spinodal dewetting. If the disjoining pressure decreases with the thickness, $\partial\Pi/\partial d < 0$, the film is stable and therefore wets the substrate, whereas it is unstable for $\partial\Pi/\partial d > 0$. The characteristic time of dewetting and the characteristic length scale of droplets depend on the slope of the disjoining pressure: $\tau \sim 12\eta\gamma/d^3/\Pi'^2$ and $\lambda \sim \sqrt{8\pi^2\gamma/\Pi'}$, where $\Pi' = \partial\Pi/\partial d$, η is the viscosity, and γ is the surface tension of the air-liquid crystal interface.[8] Therefore, by measuring these two characteristic parameters one can determine the shape of the interaction potential.

In the following, the three contributions to the disjoining pressure between the confining substrates are discussed: the van der Waals, mean-field and pseudo-Casimir force.

VAN DER WAALS FORCE

Van der Waals interaction is a common name for the dispersion interaction, which originates in the pair-wise interaction of fluctuating dipoles arising from dynamic redistribution of electrons in molecules, and the orientational interaction which results from the interaction of permanent yet fluctuating electric dipoles. The former interaction is proportional to $1/d^6$, but due to the retardation effects (which become important at distances larger than $\sim$ 5 nm) the power law approaches $1/d^7$ at $d >$ 100 nm. For materials with small permanent electric dipoles and for distances up to 100 nm the dispersion interaction dominants over the orientational one. In the nonretarded regime, the van der Waals interaction across a slab of medium j (liquid crystal) separating medium i (substrate) from medium k (air) is given by

$$\Pi_{vdW} = -\frac{A}{6\pi d^3}, \tag{2}$$

where

$$\begin{aligned} A_{ijk} &= A_{ijk}^{\nu=0} + A_{ijk}^{\nu>0} = \frac{3}{4}k_B T\frac{(\epsilon_i - \epsilon_j)}{(\epsilon_i + \epsilon_j)}\frac{(\epsilon_k - \epsilon_j)}{(\epsilon_k + \epsilon_j)} + \\ &+ \frac{3h\nu_e}{8\sqrt{2}}\frac{(n_i^2 - n_j^2)(n_k^2 - n_j^2)}{(n_i^2 + n_j^2)^{1/2}(n_k^2 + n_j^2)^{1/2}[(n_i^2 + n_j^2)^{1/2} + (n_k^2 + n_j^2)^{1/2}]}. \end{aligned} \tag{3}$$

Here ϵ's are the zero frequency dielectric permittivities of the materials, n's are their refractive indices at ν_e, and $\nu_e \sim 3 \times 10^{15}$ s^{-1} is the plasma frequency.[9] In case of a multilayer system, (such as the oxidized silicon wafer covered by 5CB, which was used in a recent experimental study of dewetting[6]), this formula becomes more complicated yet approximate, and we have calculated the van der Waals force using the complete Lifshitz theory instead.[10] As seen in Fig. 1(b), because of the dielectric properties of materials used in the experiment[6] (see Tab. I) the van der Waals force is attractive for thicknesses smaller than the

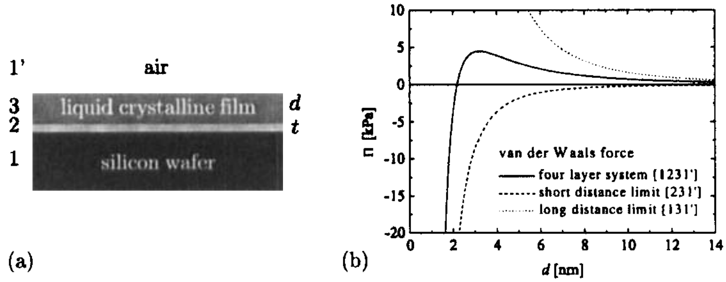


FIGURE 1 (a) Schematic representation of the liquid-crystalline deposition oxidized silicon wafer and (b) van der Waals force calculated by full Lifshitz theory (solid line) and small-*d* and large-*d* limits (dashed and dotted lines, respectively).

thickness of the absorbed layer ($d < t$) and repulsive for larger separations. The nonmonotonic behavior is due to the attractive interaction between SiO_x-liquid crystal and liquid crystal-air interfaces and the repulsive interaction between the silicon-liquid crystal and liquid crystal-air interfaces.

	Silicon (1)	Silica (2)	5CB (3)	air (1')
ϵ	12.0	14.0	17.0	1.0
n	3.5	1.5	1.6	1.0

TABLE I Zero frequency permittivity constants and refractive indices for the materials used in calculations.

STRUCTURAL FORCE

The phenomenological description of the nematic ordering is based on the tensorial order parameter Q and the associated Landau–de Gennes free energy

$$\begin{aligned} f &= \frac{L}{2}\Big\{\xi_0^{-2}\left[\theta \,\mathrm{tr}\,\mathrm{Q}^2 - 2\sqrt{6}\,\mathrm{tr}\,\mathrm{Q}^3 + (\,\mathrm{tr}\,\mathrm{Q}^2)^2\right] + \nabla\mathrm{Q}\vdots\nabla\mathrm{Q} + \\ &+ \sum_{i=P,H} \lambda_i^{-1}\,\mathrm{tr}\,(\mathrm{Q}-\mathrm{Q}_{S_i})^2\,\delta(z-z_i)\Big\}. \end{aligned} \tag{4}$$

where L is the elastic constant; θ is the reduced temperature such that $\theta = 0$ corresponds to the supercooling limit and $\theta = 1$ to nematic-isotropic phase transition temperature T_{NI}; and $\xi_0 \sim 10$ nm is the nematic correlation length at $\theta = 1$. In this parametrization, Q is scaled by the degree of the nematic order in bulk at $\theta = 1$. The last term is the surface part of the free energy density described by the tensorial analog of the Rapini-Papoular model,[11] and λ_i's are the so-called extrapolation lengths. Q_{S_i} is the preferred value of the tensor order parameter at substrate i; the substrates are located at $z_P = 0$ or $z_H = d$. In this model, the surface interaction controls both the orientation of the nematic director and the degree of nematic order. Deep in the nematic phase, the tensorial Landau–de Gennes description can be replaced by the director picture and Frank elastic formalism consisting of splay, twist, and bend deformation of the director field.[12]

The equilibrium configuration of the system is determined by the minimum of the free energy. Usually, thermal fluctuations of the order parameter are small, and their free energy can be considered a correction to the mean-field free energy. In such a case, the fluctuations of liquid-crystalline order are described consistently by harmonic Hamiltonian

$$H[b] = \frac{L}{2}\left\{\int \left[(\nabla b)^2 + \xi^{-2}b^2\right] \mathrm{d}V + \sum_{i=P,H} \lambda_i^{-1} \int b^2 \mathrm{d}S_i\right\}, \tag{5}$$

where b stands for any of the five independent fluctuating degrees of freedom of the tensor order parameter (order parameter, biaxial, and director modes)[13] and ξ is the correlation length characteristic of a particular type of fluctuations. The free energy of fluctuations is given by

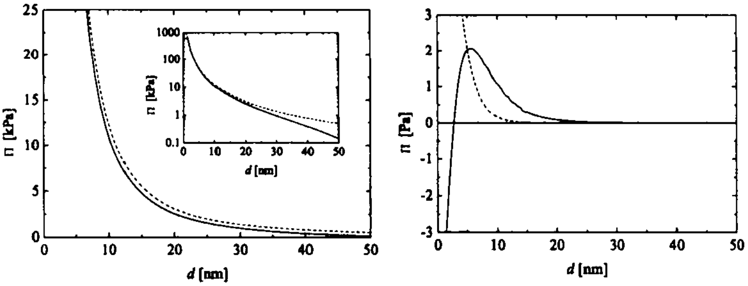
$$F_{CAS} = -k_B T \ln\left(\int \mathcal{D}b \, \exp(-H[b]/k_B T)\right), \tag{6}$$

where k_B is the Boltzmann constant and T is the temperature.[14]

In confined nematic liquid crystals there are two sources of the mean-field interaction: (i) Elastic deformations of the director field cause a long-range force in the nematic phase, whereas variations of the degree of nematic order and biaxiality result in short-range force both in nematic and in isotropic phase. (ii) In both phases, due to the restricted geometry the spectrum of fluctuations differs from the bulk spectrum, which results in additional fluctuation-induced force. Depending on the boundary conditions,[15,16] the fluctuation-induced interaction can be either repulsive or attractive; its magnitude depends strongly on the surface interaction. Generally speaking, the fluctuation modes constrained by either strong ($\lambda_{P,H} \ll d$) or weak ($\lambda_{P,H} \gg d$) anchoring at both substrates lead to an attractive force. On the other hand, the asymmetric situation with one surface enforcing strong and the other a weak anchoring yields a repulsive force.

Mean-Field Force

In a confined system, the liquid-crystalline ordering is affected by the presence of the external wall. Therefore, the free energy of the system is increased comparing



(a) (b)

FIGURE 2 Mean-field force per unit areain a typical nematic: (a) biaxial (solid line) and bent director (dashed line) structure in kPa for infinitely strong anchorings at both interfaces [$\lambda_P = \lambda_H \to 0$, $\theta = 0.9$] and (b) uniform director structure in Pa for weak anchoring at one u+interface and infinitely strong at the other interface; excess order at the free nematic surface (solid line) and no excess order (dashed line) [$\theta = 0$, $\lambda_P = 400$ nm, $\lambda_H \to 0$].

to its bulk value calculated for the system of the same volume. This thickness-dependent increase of the free energy is the source of the mean-field force between the confining substrates; the force is either attractive or repulsive.

In a hybrid nematic cell the confining substrates are characterized by mismatched easy axes, here assumed to be homeotropic and planar, respectively. Usually, dissimilar substrates differ in the anchoring strength as well. In such a system the nematic liquid crystal can be found in a variety of ordered structures.[2,17] The common feature of all ordered structures is the repulsive character of the mean-field force for separations above a few nanometers. The repulsion is due to the antagonistic boundary conditions which always lead to at least small deformation. The magnitude of the force is tuned by the anchoring strength at both substrates whereas its functional form depends on the structure in question (Fig. 2). On the contrary, it is known that the mean-field force in a non-frustrating nematic geometry is always attractive.[18]

From the Frank elastic theory the dependence for the bent-director structure is known to be roughly given by $\Pi \propto 1/d^2$, where d is the film thickness [Fig. 2(a)]. Within the same theory there is no mean-field force for the uniform director structure below the critical film thickness, $d_c = |\lambda_P - \lambda_H|$. Taking into account all five degrees of freedom of the nematic order one can determine the non-zero mean-field contribution to the structural force [Fig. 2(b)]. Depending on the details of the induced order the force can be either repulsive or can exhibit a nonmonotonic behavior characterized by attraction at small d's. The latter case corresponds to the substrates that induce higher order than characteristic for the given temperature, e.g., the excess order at the free surface of some nematic liquid crystals.[19] Here the turn-over between the regime of the increasing and decreasing force with the increasing film thickness is related to the fact that above certain film thickness the order at the side with stronger anchoring is above its bulk value whereas it is below it on the other side. The magnitude of that force is typically two orders of magnitude smaller comparing to the one in the bent-director case and does not play important role in the stability of the film.

To complete the description of the mean-field force let us mention the mean-field force in the biaxial structure. This force is repulsive and exhibits $1/d^2$ behavior at small thicknesses whereas at large d's the exponent of the power law is smaller than -2 [Fig. 2(a)]. The decrease of the range of the force is a consequence of the localization of the deformation when approaching the stability limit of this structure.[2]

Pseudo-Casimir Force

In the vicinity of the clearing point, the equilibrium ordering in thin cells is biaxial and highly inhomogeneous.[2] On the other hand, deep in the nematic phase and for samples thicker than few nematic correlation lengths the degree of nematic order is almost uniform and uniaxial, whereas the director field can be either bent ($d > d_c$) or uniform ($d < d_c$). In this review, we limit the analysis of pseudo-Casimir force to films thick enough for the ordering to be consistently described by the director. We assume that the homeotropic anchoring is stronger than the planar anchoring so that the uniform structure is homeotropic.

The free energy of the two director modes is determined by the partition function [Eqn. (6)] (for details of the calculation see Ref. [4]). Neglecting non-director degrees of freedom the pseudo-Casimir force depends on the temperature and extrapolation lengths

$$\Pi = -\frac{k_B T}{d_c^3}\,\frac{1}{2\pi}\left(\frac{K_{33}}{K_{11}} + \frac{K_{33}}{K_{22}}\right)\int_0^\infty \frac{p^2 \mathrm{d}p}{\frac{p-1+\Lambda}{p+1-\Lambda}\frac{p+\Lambda^{-1}-1}{p-\Lambda^{-1}+1}\mathrm{e}^{2px} - 1}, \tag{7}$$

where K_{ii} are the elastic constants related to the splay, twist and bend deformations, k_B is the Boltzmann constant, $\Lambda = \lambda_H/\lambda_P$, and $x = d/d_c$. The above expression can not be calculated analytically except in a few limiting cases. For the finite but similar extrapolation lengths ($\Lambda \to 1$) the force is attractive and decreases as d^{-3} which is a typical behavior for equal boundary conditions,[15,16]

$$\Pi\,(\Lambda \to 1) \approx -\frac{\zeta(3)}{8\pi}\left(\frac{K_{33}}{K_{11}} + \frac{K_{33}}{K_{22}}\right)\frac{k_B T}{d^3}, \tag{8}$$

where ζ is the Riemann zeta function. In the case of infinitely strong homeotropic anchoring ($\Lambda \to 0$) the system reduces to mixed boundary conditions for the

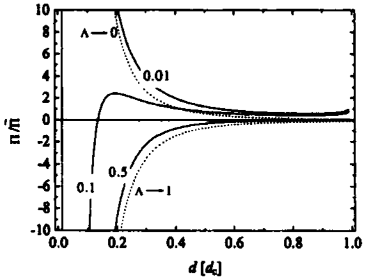


FIGURE 3 Pseudo-Casimir force for different values of $\Lambda = \lambda_H/\lambda_P$; $\tilde{\Pi} = (k_BT/2d_c^3)(K_{33}/K_{11} + K_{33}/K_{22})$.

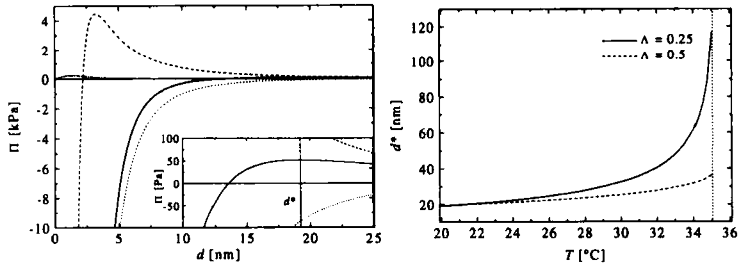
fluctuating modes, resulting in a d^{-3} repulsion[15,16]

$$\Pi(\Lambda \to 0) \approx \frac{3\zeta(3)}{32\pi}\left(\frac{K_{33}}{K_{11}} + \frac{K_{33}}{K_{22}}\right)\frac{k_BT}{d^3}. \tag{9}$$

In real hybrid systems with both λ_P and $\lambda_H > 0$, the fluctuation-induced force is attractive at small d/d_c's, then it becomes repulsive and may reach a local maximum before the pretransitional singularity, which is common for all combinations of extrapolation lengths in the hybrid geometry.[4] At very small thicknesses ($d/d_c \ll 1$) both extrapolation lengths are larger than the thickness of the cell, therefore both surface interactions are effectively weak resulting in an attractive pseudo-Casimir interaction. On increasing the distance, the fluctuation-induced force becomes repulsive when the homeotropic extrapolation length becomes smaller than the cell thickness: for $\lambda_H < d < \lambda_P$, the homeotropic anchoring is strong whereas the planar anchoring is weak [Fig. 3].

DISJOINING PRESURE

The disjoining pressure refers to the total force between the confining substrates per unit area. As seen in Fig. 4, depending on the temperature the disjoining pressure is attractive for thicknesses up to 10-100 nm, whereas it is repulsive elsewhere. However, it is not the sign of the force that determines the stability of the film but rather the sign of its derivative, i.e., $\partial\Pi/\partial d$. As mentioned above, in real liquid-crystalline depositions the air-liquid crystal interface fluctuates due to thermal capillary waves. These waves destabilize the film if $\partial\Pi/\partial d > 0$ ($d < d^*$). The unstable and stable regimes are separated by a marginal thickness d^* [Fig. 4(a)]. As we have shown, van der Waals, mean-field, and pseudo-Casimir force can all exhibit this kind of behavior. However, the marginal thickness for the van der Waals force is in the range of few nm whereas the observed marginal



(a) (b)

FIGURE 4 (a) Disjoining pressure within the liquid crystal in contact with a solid substrate and air (solid line) deep in the nematic phase. The dashed line corresponds to van der Waals force, whereas the dotted and dash-dotted lines depict the pseudo-Casimir and mean-field contributions, respectively. Inset: behavior of the disjoining pressure in the vicinity of the marginal thickness. (b) Temperature dependence of the marginal thickness for different Λ's.

thicknesses are an order of magnitude larger.[6] The correction due to the non-zero mean-field contribution is very small and slightly decreases the marginal thickness. On the other hand, the observed marginal thickness can be reproduced by including the pseudo-Casimir force. This proves that the pseudo-Casimir force plays a crucial role in the spinodal dewetting and the corresponding experiments can be thought of as a first experimental evidence of the fluctuation-induced force in liquid crystals.

Modeling the temperature dependence of the extrapolation lengths as $\lambda_i \propto Q^{-2}(T)$,[20] where $Q(T)$ is the bulk degree of nematic order one can get the temperature dependence of the marginal thickness. Fig. 4 (b) shows the predicted temperature dependence for different values of Λ.

CONCLUSIONS

In this paper, we summarized the results of our recent theoretical studies of structural forces in thin hybrid nematic films and the stability of these films. We showed that in highly frustrated geometries the structural forces, originating in deformed nematic ordering and modified spectrum of fluctuations, can play an important role in the stability of the film. The confinement-induced features of the film are especially prominent in the vicinity of structural transitions. Some of the effects discussed have been observed in a study of spinodal dewetting of 5CB on a silicon substrate.[6] Further experiments are expected to reveal the shape of the interaction potential in more detail.

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References

[1] P. Ziherl, A. Šarlah, and S. Žumer, Phys. Rev. E **58**, 602 (1998).
[2] A. Šarlah and S. Zumer, Phys. Rev. E **60**, 1821 (1999).
[3] H. B. G. Casimir, Proc. Kon. Ned. Akad. Wet. **51**, 793 (1948).
[4] P. Ziherl. F. Karimi Pour Haddadan, R. Podgornik, and S. Zumer, Phys. Rev. E **61**, 5361 (2000).
[5] P. Ziherl, R. Podgornik, and S. Žumer, Phys. Rev. Lett. **84**, 1228 (2000).
[6] S. Herminghaus, K. Jacobs, K. Mecke, J. Bischof, A. Fery, M. Ibn-Elhaj, and S. Schlagowski, Science **282**, 916 (1998); F. Vandenbrouck, M. P. Valignat, and A. M. Cazabat, Phys. Rev. Lett. **82**, 2693 (1999).
[7] P. Ziherl, Phys. Rev. E **61**, 4636 (2000).
[8] F. Brochard Wyart and J. Daillant, Can. J. Phys. **68**, 1084 (1990).
[9] J. Israelachvili, *Intermolecular & Surface Forces* (Academic Press, London, 1985).
[10] J. Mahanty and B. W. Ninham, *Dispersion Forces* (Academic Press, London, 1976).
[11] M. Nobili and G. Durand, Phys. Rev. A **46**, R6174 (1992).
[12] F. C. Frank, Discuss. Faraday Soc. **25**, 19 (1958).
[13] P. Ziherl and S. Zumer, Phys. Rev. Lett. **78**, 682 (1997).
[14] P. M. Chaikin and T. C. Lubensky, *Principles of condensed matter physics* (Cambridge University Press, Cambridge, 1995).
[15] A. Ajdari, L. Peliti, and J. Prost, Phys. Rev. Lett. **66**, 1481 (1991); A. Ajdari, B. Duplantier, D. Hone, L. Peliti, and J. Prost, J. Phys. II (Paris) **2**, 487 (1992).
[16] H. Li and M. Kardar, Phys. Rev. Lett. **67**, 3275 (1991); H. Li and M. Kardar, Phys. Rev. A **46**, 6490 (1992).
[17] O. D. Lavrentovich and V. M. Pergamenshchik, Mol. Cryst. Liq. Cryst. **179**, 125 (1990); O. D. Lavrentovich and V. M. Pergamenshchik, Phys. Rev. Lett. **73**, 979 (1994).
[18] A. Borštnik and S. Žumer, Phys. Rev. E **56**, 3021 (1997).
[19] E. Martin del Rio, M. M. Telo da Gama, E. de Miguel, and L. F. Rull, Europhys. Lett. **35**, 189 (1996); H. Kasten and J. Strobl, J. Chem. Phys. **103**, 6768 (1995).
[20] A. Mertelj and M. Čopič, Phys. Rev. Lett. **81**, 5844 (1998).