Capillary instabilities by fluctuation induced forces

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Abstract. The spontaneous break-up of thin films is commonly attributed to the destabilizing effect of van der Waals forces. Dispersion forces can be considered in terms of the confinement of the electromagnetic fluctuation spectrum. The principle of confinement is more general than the usual argument of interacting dipole fluctuations. It includes also disjoining pressures that are caused by thermal fluctuations. In this context, we review recent publications on the dewetting of thin polymer films, and argue that the presence of an acoustic disjoining pressure is necessary to adequately describe some of these experimental results.

PACS. 47.20.Ma Interfacial instability - 68.15.+e Liquid thin films - 43.25.Qp Radiation pressure

1 Introduction

The study of capillary instabilities and their causes goes back more than one century [1]. While the destabilization of planar liquid surfaces on a macroscopic scale requires an externally applied potential (such as electric or magnetic fields [2]), thin films are known to become spontaneously unstable. This was explained by Vrij [3], Scheludko [4], Ruckenstein and Jain [5], and others in terms of the destabilizing effect of a disjoining pressure that is caused by dispersive (van der Waals) forces. Recently, this topic was rediscovered, leading to a flurry of publications on the dewetting of thin polymer films [6,7], liquid metals [8], etc. This renewed interest was not only caused by the technological importance of film stability (e.g. for coatings, lubrication layers, etc.), but also because liquid dewetting leads to a rich pattern formation process.

A further important aspect concerns the fundamental character of capillary instabilities themselves. As opposed to liquid columns, planar surfaces are stabilized by the surface tension. Patterns created by a capillary instability are therefore characteristic for the force driving the instability. In terms of the recent experiments on the dewetting of thin polymer films, this aspect received only little attention. This is partially due to experimental complications. For highly viscous polymer melts, capillary instabilities driven by van der Waals (vdW) forces are slow and films often break up by heterogeneous nucleation [6] before the onset of a so-called spinodal instability [7]. A second reason for the lack of systematic studies is the seemingly obvious nature of their outcome: capillary instabilities should reflect the destabilizing nature of dispersive vdW forces predicted more than 50 years ago [3-5].

It is therefore surprising that most experimental studies that quantitatively analyze capillary instabilities of thin polymer films find discrepancies of varying degrees. The apparent problem to obtain reliable data reflects at the same time the strength of these experiments: the spectrum of spontaneously amplified capillary waves is very sensitive to the detailed force balance acting at the surface of the film. While this poses a considerable challenge for the experimenter, the stability of thin films can be used as a sensitive tool to explore surface and interfacial forces in detail. The discrepancies between experiments and models based solely on van der Waals forces therefore stem most likely from the presence of additional destabilizing potentials. Possible additional destabilizing effects may arise from the polar nature of the confining medium [9, 10], the presence of electric charges [11], applied electric fields [12,13] or temperature gradients [14,15], stresses induced by the substrate [16] or stabilizing capping layers [17], etc.

In this commentary, we regard van der Waals driven film instabilities from a somewhat unusual angle and propose a generalization that leads to an equivalent disjoining pressure caused by the confinement of thermal noise. This discussion extends a recent publication on the same topic [18]. First, we discuss the relevance of the thermoacoustic disjoining pressure for various experimental approaches. Second, in the absence of a clear-cut experimental verification, we present model calculations, indicating the route for the experimental confirmation of this effect.

2 Fluctuation induced forces

In 1948, Casimir [19] considered the electromagnetic quantum fluctuation of vacuum in a cavity of width ℓ formed by two conducting plates. While the sum of ground state

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energies is infinite, there is a finite energy difference per plate unit area S, compared to the unconfined case [20]

$$\frac{\Delta E}{S} = -\frac{\pi^2}{720} \frac{\hbar c}{\ell^3}.$$
 (1)

The dependence of ΔE on the distance between the two conducting surfaces implies an attractive force. The nature of this force is purely entropic: the reduction of the space between the two plates and thereby the enlargement of the unconfined external space maximizes the number of allowed electromagnetic modes.

As a generalization of the so-called Casimir effect, the van der Waals-London forces [21] can be understood in an analogous argument [22]. The change in the mode spectrum of two harmonic oscillators with eigenfrequency ω and polarizability α , brought from infinity to a distance ℓ corresponds to an energy change

$$\Delta E \approx -\hbar \omega \frac{\alpha^2}{\ell^6}.$$
 (2)

Equation (2) is equivalent to the original description by London [21], which is based on a different physical argument. The usually adopted viewpoint of dispersive interactions invokes the interaction of dipole fluctuations. The classic argument assumes a dipole fluctuation of a neutral atom, inducing a dipole moment in a second atom at distance ℓ . While the time-averaged dipole moments of both atoms are zero, the mean attractive energy based on the attraction of the two instantaneous dipoles is finite, giving rise to the van der Waals attraction. Both descriptions, which seem to have little in common lead to the same expression (Eq. (2)). The generalization to a slab of dielectric medium 3 bounded by semi-infinite media 1 and 2 leads to the well known van der Waals energy for both the London and Casimir formalism [23]

$$\frac{\Delta E_{\rm vdW}}{S} = -\frac{A_{132}}{12\pi\ell^2} \tag{3}$$

introducing the Hamaker constant A_{132} . According to the Lifshitz theory [23]

$$A_{132} \approx \frac{3}{4} kT \left(\frac{\varepsilon_1 - \varepsilon_3}{\varepsilon_1 + \varepsilon_3}\right) \left(\frac{\varepsilon_2 - \varepsilon_3}{\varepsilon_2 + \varepsilon_3}\right) + \frac{3h\nu_{\rm e}}{8\sqrt{2}} \frac{\left(n_1^2 - n_3^2\right)\left(n_2^2 - n_3^2\right)}{\sqrt{n_1^2 + n_3^2}\sqrt{n_2^2 + n_3^2}\left(\sqrt{n_1^2 + n_3^2} + \sqrt{n_2^2 + n_3^2}\right)}$$
(4)

with the dielectric constants ε_i and refractive indices n_i of the three media, and $h\nu_e$ the energy corresponding to the main electronic UV absorption frequency ν_e .

The advantage of the Casimir over the London description is its wider scope. The entropy argument is equally valid for any fluctuation spectrum. In analogy with the electromagnetic Casimir effect, there is a finite energy associated with the long-wavelength cut-off imposed by a geometrical confinement of any type of noise. While fluctuation induced disjoining pressures include examples in cosmology, atoms in cavities, inclusions in membranes, and correlated fluids [20,22], we focus our attention on thermal fluctuations. On purely dimensional grounds, one expects a contribution to the free energy due to the confinement of acoustic modes in a slab geometry of

$$\frac{\Delta E}{S} \approx -\frac{kT}{\ell^2}.$$
(5)

In a more detailed argument [18], one finds

$$\frac{\Delta E_{\rm ac}}{S} = -\frac{\pi}{36} \frac{kT}{\ell^2}.$$
(6)

Equations (3) and (6) are formally quite similar. Since for organic films on common substrates at ambient temperatures $|A_{132}| \sim kT$ [23], $\Delta E_{\rm ac}$ and $\Delta E_{\rm vdW}$ should be on the same order of magnitude.

The derivative of ΔE with respect to the film thickness leads to the electromagnetic and acoustic disjoining pressures $p_{\rm vdW}$, $p_{\rm ac}$. Depending on their sign $p_{\rm vdW}$ and $p_{\rm ac}$ may destabilize the film, resulting in a maximally unstable mode [18]

$$q_{\rm m}^2 \propto \frac{1}{2\gamma} \frac{\partial}{\partial \ell} \left(p_{\rm vdW} + p_{\rm ac} \right) \tag{7}$$

that can be experimentally determined by measuring the wavelength of the film instability $\lambda = 2\pi/q_{\rm m}$.

Before we discuss the relative role of the electromagnetic and acoustic disjoining pressures, it is important to discuss the limitations of equation (6). As opposed to equation (3), which applies to any combination of dielectric materials 1, 2, 3 (the materials dependence is contained in A_{132}), the validity of equation (6) is limited to the case of no coupling of the acoustic modes of medium 3 (the film) to the adjacent media 1 and 2. This implies a large difference in acoustic impedance between medium 3 and 1, 2. A second requirement applies to fluctuation induced forces in general: only modes with a mean-free path length greater than than the confinement ℓ give rise to a confinement induced disjoining pressure. For polymer melts, acoustic modes with a wavelength of ~ 100 nm, have a mean free path length of several micrometers [24].

3 The experimental situation

As becomes clear from a comparison of equations (3) and (6), polymer film stability is governed by the interplay of disjoining pressures of electromagnetic and acoustic origins. This implies not only that both contributions have to be taken into account when analyzing data from film instabilities, but could also lead to effects that cannot be explained on the basis of electromagnetic effects alone [18]. While quantitative data on polymer film instabilities are relatively sparse, we review four different published cases in the light of the previous section.

3.1 Free standing polymer films

The theoretically most simple case is the stability of a free standing film. Here, both $p_{\rm vdW}$ and $p_{\rm ac}$ enhance

capillary surface waves and therefore destabilize the film. Experimentally, unstable free standing films are difficult to study. In an elegant approach, Dutcher et al. [17] have stabilized liquid polystyrene (PS) films with thin solid capping layers. This prevents a complete disintegration of the unstable PS films, thereby facilitating the investigation of the instability. For the parameters of their experiment $(A_{\rm PS} = 6.5 \times 10^{-21} \text{ J}, T = 210 \text{ °C}), p_{\rm vdW} \approx 3p_{\rm ac}$. This should lead to a rather small contribution ($\approx 10\%$) of the measured instability wavelength. The contribution of $p_{\rm ac}$ does not account for the big discrepancy between data and theory reported in [17]. The fitted value of $A_{\rm PS}$, which is too large by a factor of 2400 possibly originates from thermally induced stresses in the capping layers [25].

3.2 Polymer films on solid substrates

By far the most common experiments involve liquid polymer films on solid substrates. Since typical substrates (silicon, glass, metals) have much higher acoustic impedances and elastic moduli, there is only little coupling between the acoustic modes in the film and the substrate. Therefore, $p_{\rm ac}$ destabilizes the film. The sign of the Hamaker constant (Eq. (4)) and therefore the sign of $p_{\rm vdW}$ depends mainly on the refractive index of the substrate n_1 compared to the film n_3 . PS on silicon $(n_1 > n_3)$ is stabilized by $p_{\rm vdW}$, while PS on glass $(n_1 < n_3)$ is unstable. The interplay between stabilizing and destabilizing components of $p_{\rm vdW}$ was shown by Seemann et al. [26] for PS on Si substrates covered by oxide layers of varying thickness. On such composite surfaces, thin PS films are unstable, while thicker layers are stable. For a PS film thickness comparable to the dimension of the oxide layer, $p_{\rm vdW}\approx 0$ and the film instability should be dominated by p_{ac} . The data in [26] is quantitatively better explained by the inclusion of $p_{\rm ac}$ in the data analysis, compared to a model based on p_{vdW} alone [18].

3.3 Polymer films on polymer substrates

Capillary instabilities were also observed for polymerpolymer interfaces [27]. Sferrazza and coworkers [28] quantitatively studied the instability of polymethylmethacrylate (PMMA) films supported by a (liquid) PS substrate. They interpret the results of their neutron reflectivity study in terms of a capillary instability of the PMMA-PS interface and determine a Hamaker constant according to equation (7). Their results are surprising, however, since the negative sign of the experimentally determined and theoretically predicted (Eq. (4)) Hamaker constant corresponds to a stable PMMA film. To attribute the PMMA film instability to a dominance of $p_{\rm ac}$ is equally unlikely, since PS and PMMA have very similar acoustic properties. The coupling of the acoustic modes of the PMMA film and the thick PS substrate significantly reduce the confiment of thermo-acoustic modes.

3.4 Polymer films at the substrate-water interface

The best studied system is polydimethylsiloxane (PDMS) films, deposited onto silicon wafers, covered by water [9,10]. These experiments result in film instabilities that can be accounted for by assuming a Si-PDMS-water Hamaker constant that is too large by 2-3 orders of magnitude. Similar to PMMA on PS, we expect $p_{\rm ac}$ to be negligible, due to a significant acoustic coupling of PDMS and water. The large discrepancy between experiments and theory could arise from the polar nature of water, requiring a more detailed model for the calculation of the Si-PDMS-water Hamaker constant [9].

4 Film destabilization by the confinement of thermal fluctuations

The rather large deviations between the experimental data and predictions make it difficult to distinguish between the contribution of van der Waals and acoustic disjoining pressures. Conceptually, we expect $p_{\rm ac}$ to become important in the case of free-standing or supported polymer films. From equations (3) and (6), $|p_{\rm ac}| > |p_{\rm vdW}|$ for $|A_{132}| < \pi^2/3kT$. This implies $|A_{132}| < 1.3 \times 10^{-20}$ J at room temperature and $|A_{132}| < 2 \times 10^{-20}$ J for $T \approx 170$ °C. An unambiguous experimental verification of the presence of an acoustic disjoining pressure therefore necessitates the choice of a system with low values of $|A_{132}|$ and suitable mechanical boundary conditions. We discuss here three possible experiments to verify the presence of a disjoining pressure arising from the confinement of thermally excited acoustic modes.

4.1 Marginally van der Waals stabilized films

The basic idea of this class of experiments is to choose a supported film system, in which $p_{\rm vdW}$ acts to stabilize the film, but is overpowered by a destabilizing $p_{\rm ac}$. Using the argument outlined above, this implies $-1.3 \times 10^{-20} \,\mathrm{J} < A_{132} < 0$. Since the Hamaker constant is primarily governed by the refractive indices n_i of the three media, this implies a choice of $n_1 \gtrsim n_3$ (where 1 and 3 refer to the substrate and film, respectively).

In Figure 1 we show the result of a linear stability analysis [29] of two polymer-substrate combinations that are expected to be marginally stable in terms of their van der Waals energy, but should be unstable if $p_{\rm ac}$ is taken into account. Figure 1a shows the maximally unstable mode of PMMA ($n_{\rm PMMA} = 1.49$) on a microscopy glass slide (white glass: $n_{\rm glass} = 1.50$). The predicted value of $A_{132} = -1.48 \times 10^{-21}$ J leads to a stabilizing effect of $p_{\rm vdW}$, which is one order of magnitude smaller compared to $p_{\rm ac}$. A complementary second system is PDMS ($n_{\rm PDMS} = 1.40$) on SiO₂ ($n_{\rm SiO_2} = 1.46$), shown in Figure 1b ($A_{132} = -6.22 \times 10^{-21}$ J).

The appeal of these experiments is the qualitative effect that should be observable, i.e. the observation of an instability of a film that is expected to be stable if only vdW forces are considered.



Fig. 1. Instability wavelength λ vs. film thickness ℓ for (a) PMMA (n = 1.49) on glass (n = 1.5) and (b) PDMS (n = 1.4) on SiO₂ (n = 1.46). The presence of a film instability is a signature of $p_{\rm ac}$, since vdW forces stabilize the film. The solid, dotted and dashed lines in (a) correspond to temperatures of 50 °C, 90 °C, and 170 °C, the solid, dashed and dash-dotted lines in (b) correspond to temperatures of 50 °C, 170 °C, and 270 °C, respectively.



Fig. 2. Instability wavelength λ vs. film thickness ℓ for PS on composite substrates. (a): PS on Si covered by 1.6 nm (\blacksquare) and 3.5 nm (\blacktriangle) thick SiO_x layers. (b): PS on MgF₂ covered by 0.5 nm (\blacksquare) and 2 nm (\bigstar) thick Si₃N₄ layers. On the stabilizing substrate in (a), the curves diverge for $\ell > \ell_c$, while on the destabilizing substrate in (b), the stabilizing Si₃N₄ layer introduces a lower cut-off in ℓ , below which the film should be stable. The dashed and dash-dotted lines correspond to the assumption $p_{\rm ac} = 0$.

4.2 Film instabilities on composite substrates

This approach was introduced in a recent study by the Ulm group [26]. They use a substrate on which a polymer film is stable. If the substrate is covered with a thin layer of a material that has a destabilizing effect on the film, a partial compensation of stabilizing and destabilizing vdW disjoining pressures is achieved. In particular, there is a critical polymer film thickness ℓ_c , at which $p_{vdW} = 0$. This is reflected in the stability diagram of the film (Fig. 2a), showing a spinodal instability for $\ell < \ell_c$ and metastable films for $\ell > \ell_c$. As shown by us earlier, a finite value of p_{ac} shifts ℓ_c to larger film thicknesses, in agreement with the data in [26].

The repetition of this kind of study encompassing a large number of experimental systems should reveal, whether there is a systematic shift of ℓ_c , which should be independent of the optical dispersion of the three materials. Such a systematic shift, would be a clear signature of a



Fig. 3. Instability wavelength λ vs. film thickness ℓ for PS on a Si substrate covered by a 1.6 nm thick SiO_x layer. The contribution of the vdW pressure (assuming $p_{\rm ac} = 0$) shows a negligible variation with temperature (dashed lines). This is opposed to the case, where $p_{\rm ac}$ was included in the model calculation. For the three temperatures 50 °C (\blacksquare), 90 °C (\blacktriangle), and 170 °C (\blacklozenge), a detectable variation of ℓ_c is predicted.

disjoining pressure stemming from acoustic fluctuations. Typical examples are shown in Figure 2.

4.3 Temperature dependence of film instabilities

A third experimental approach is based on the system described in Section 4.2. Since the Hamaker constant is only weakly temperature dependent (i.e. the dielectic constants and the refractive indices change only little with temperature), it is possible to infer information about the presence of $p_{\rm ac}$ from the temperature dependence of ℓ_c , shown in Figure 3. Taking both the variation of surface tensions and Hamaker constants into account, one expects a negligible variation of ℓ_c , based on a calculation that takes only $p_{\rm vdW}$ into account. The effect of an inclusion of $p_{\rm ac}$ in the model should result in a small, but experimentally discernible variation of ℓ_c .

4.4 Retardation effects

With increasing values of ℓ there is a decrease in correlations of confined electromagnetic modes, or, in the London model, a decrease in correlation in dipole-dipole interactions. For sufficiently large values of ℓ $(c/(2\pi\nu_e) \ll$ $\ell \ll hc/(2\pi kT)$), equation (3) must be replaced by a rela-tion $\Delta E_{\rm ret} \propto \ell^{-3}$. Equation (6), on the other hand, stays unchanged (assuming that the mean free path length of acoustic modes is still large compared to the film thickness). Due to the relatively short correlation length of acoustic modes at ambient temperatures, the acoustic modes were assumed to be uncorrelated in the derivation of equation (6) [18]. In terms of equation (7), this implies a dominance of $p_{\rm ac}$ over $p_{\rm vdW}$ for $\ell\gtrsim 100$ nm. While this leads to interesting predictions for large values of ℓ (e.g. reentrant instabilities [18]), instabilities of thick films are experimentally difficult to study. Since the characteristic time constant associated with capillary instabilities scale with ℓ^4 , they are typically preempted by the heterogeneous nucleation of holes in thick films [6]. Experiments exploiting the change in the balance of retarded electromagnetic and thermo-acoustic modes, require a liquid film with a low surface tension and a low viscosity (e.g. low molecular weight PDMS).

5 Conclusions

When discussing the origin of the disjoining pressure from the view-point of the confinement of a fluctuation spectrum, it becomes clear that not only electromagnetic effects (leading to a van der Waals disjoining pressure), but also thermally excited acoustic fluctuations play a role in the destabilization of thin films. Since the Hamaker constants are on the order kT for typically studied thin film systems and temperatures, the acoustic disjoining pressure is not negligible. Whether it contributes to thin film instabilities depends on a number of parameters. It is expected to be significant in the case of supported films, in particular for the much studied case of PS on Si, covered by 1–3 nm thick oxide layers.

While predicted to be important for the interpretation of dewetting experiments, the unambiguous detection of the confinement of acoustic modes is not simple. Since $p_{\rm ac}$ and $p_{\rm vdW}$ have the same dependence on the film thickness ℓ , only quantitative measurements will allow to distinguish the two effects. The experimental systems described in Section 4 are conceptually simple, but require high precision measurements. Film and surface layer thicknesses must be determined with a sub-nanometer precision, while an accuracy of ≈ 100 nm is necessary for the determination of the instability wavelength. This requires carefully conducted experiments, and a combination of ellipsometry and atomic force microscopy as experimental techniques.

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Discussion on contribution by U. Steiner

Comment by P. Ziherl and S. Zumer

The paper deals with the force induced by acoustic or density fluctuations as a universal interaction between the interfaces of a film. This is an extremely interesting point. It seems it would be worthwhile exploring the analogy with the van der Waals force in some detail. To a layman, it seems that the sign of the force could be predicted by comparing the speed of sound in the three media. Then the acoustic Casimir force should stabilize a polymer film on a solid substrate since the speed of sound is largest in the substrate and smallest in air (which would imply a repulsive force). This is inconsistent with the statement in Section 3.2.

Steiner replies

I agree with your statement that the acoustic disjoining pressure could, in principle have both signs. Whether or not there is a physical system, in which this can be observed is an entirely different question. Let me explain.

First of all, we assume that the acoustic spectra of all three media are decoupled. Then it is unfavorable to intercalate a film of any material (irrespective of the velocity of sound in the film) at the interface of two media, since the number of modes in the unconfined media is always larger than in the confined medium. In the case of a polymer film on a solid substrate this is a reasonable assumption, since the elastic modulus of the film is very different from the adjacent media (e.g. there are no coupled modes) – the elastic moduli of hard substrates and polymers differ typically by two orders of magnitude or more. Long wavelength acoustic modes in the film have therefore a node at the substrate-film interface and a free boundary at the film-air interface.

More general is of course the case, in which the three materials have more similar acoustic properties. In this case, the mode spectra of the three media are coupled. We have not calculated this case, which I expect to be mathematically somewhat complex. On a qualitative level, I agree with you that, in analogy with the electromagnetic case, it is likely that both signs can be obtained. At the same time, the effect should become much weaker, since film modes that couple to the surrounding media are less effectively confined. In such case, it is likely that a substrate-film-air system with acoustic impedances going from high (substrate) to low (air) has a stabilizing acoustic disjoining pressure, whereas a film with a higher acoustic impedance than the surrounding media should be destabilized by the acoustic disjoining pressure. Even if there were a proper theoretical prediction of this effect, it will be an even higher challenge to measure this experimentally, since the acoustic disjoining pressure should be very small, and should therefore be even more easily overpowered by van der Waals forces of other residual forces in the film.

To carry the analogy with electromagnetic theory a bit further. Our prediction and suggestion for experiments should be compared to Casimir's original work of an air gap between two conducting plates. In such a case there is no coupling between the electromagnetic modes "inside" and "outside". The generalization to the general case of van der Waals forces was done (among others) by Dzyaloshinskii, Lifshitz and Pitaevskii. We need the acoustic equivalent to the Dzyaloshinskii, Lifshitz and Pitaevskii calculations to predict the acoustic disjoining pressure in the most general case.

Comment by H. Kaya and B. Jérôme

The presence of a universal acoustic force creating an additional disjoining pressure is certainly an important issue. As the authors themselves point out, however, the acoustic and van der Waals energy terms have the same dependence on the film thickness, thus making it difficult to separate the two contributions. The acoustic part of the disjoining pressure can be incorporated in an effective Hamaker constant by $A_{eff} = A_{132} + \pi^{2/3}$ kT. This added constant indicates that Hamaker constants calculated from typical length scales in dewetting experiments, are systematically too high.

To search for additional destabilizing potentials can be unnecessarily complicating. As we point out in our contribution [32], even apparently simple modifications of the basic van der Waals potential can easily lead to complicated expressions for the corresponding disjoining pressure and spinodal parameter.

U. Thiele comments on statements from the contribution

"Patterns created by a capillary instability are characteristic for the force driving the instability".

"The spectrum of spontaneously amplified waves is very sensitive to the detailed force balance acting at the surface of the film".

The first statement is certainly true because it refers to the full nonlinear patterns (and their evolution) resulting from the surface instability. So can, for example, the driving potential or force be reconstructed from the profile of a drop (best from a micro- or nanodrop).

However, the second statement refers to the spectrum of amplified waves, i.e. to the linear behaviour. This is covered by a dispersion relation of the form $\beta = -k^2(k^2 - k_c^2)$ independently of the specific acting forces. The latter only determine the length scale $1/k_c$ and the time scale $1/\beta$ of the instability. The form of the dispersion relation is solely determined by the form of the evolution equation for the film thickness. This form is generic for the evolution equation for an conserved order parameter field [J.S. Langer, in, *Solids far from equilibrium*, edited by C. Godreche (Cambridge University Press, 1992), pp. 297–363]. However, I certainly agree on that in the present state of knowledge even the length scale given by the wave number of the fastest growing linear mode $k_m = k_c/\sqrt{2}$, its dependence on system parameters like film thickness or temperature, and instability thresholds like critical film thicknesses (where $k_c = 0$) are good tools to test existing theories.

U. Steiner adds some additional information on statements in his contribution

Patterns created by a capillary instability are characteristic for the force driving the instability.

1. The amplification of a part of the capillary wave spectrum requires a destabilizing force. The experimental observation of a surface instability (either the wave itself, of the bicontinuous pattern that is left after a film instability) is therefore evidence for the presence of a destabilizing force. The question is therefore (1) is it possible to prepare a system in a way that only a single force (or quantifiable sum of forces) causes the film instability, and (2) is it possible to deduce form the film instability the nature of this force (or sum of forces). The answer to (1)has to do with the usual problem an experimentalist has to face: yes, it is usually possible to eliminate known effects, that are not of interest in a specific investigation. This leaves the problem, that still unknown causes distort the experimental results. It is part of the scientific process, to identify those causes – this is precisely what we are doing here. The answer to (2): by systematically varying parameters on which the destabilizing force depends, it should be possible to identify the force. A good example of this is the Seemann-Jacobs-Herminghaus paper (Phys. Rev. Lett. 86, 5534 (2001)

2. While the amplification of part of the capillary wave spectrum is the sign of the presence of a destabilizing force, the opposite conclusion is incorrect, since it is well known that heterogeneous nucleation can preempt a capillary instability (see for example the contribution of O.K.C. Tsui et al. [32]).

The spectrum of spontaneously amplified waves is very sensitive to the detailed force balance acting at the surface of the film.

In the sense described above, this statement is correct. The force balance is "sensitive" in a sense, that the wavelength of the initially amplified mode mirrors the magnitude of the force gradient. At this point hydrodynamics does not (yet) come into play, nor do secondary effects such as the combination of a capillary instability and nucleation, as discussed by U. Thiele [33].

Is it sufficient to search for additional destabilizing potentials or do we also need to pay more attention to the kinetics of the destabilisation processes (how fast the various processes evolve and contribute to destabilisation)?

The paper focuses on qualitative effects. In particular the observation of a capillary instability of a film on a substrate, on which it should be stabilized by a van der Waals disjoining pressure should yield information about the sign of the overall disjoining (or conjoining) pressure. The question about kinetics is of secondary importance in this case. The sample applies to the proposed experiments, in which only the acoustic boundary conditions are changed. The experiments that make use of the temperature dependence are a bit more tricky, since in these experiments changes in the break-up kinetics (beyond the temperature dependence of the Hamaker constant and the surface tension) may com into play.

Are the proposed experiments on meta-stable films (= films stabilized by van der Waals forces but on nonwettable substrate) doable and can they be interpreted unambiguously? Are other sources for destabilisation (density variations) likely to intervene?

It is essential that this type of experiments are done very carefully. It is for example important to pre-anneal the films, to make sure that they are as solvent and stress free as can be achieved. Density gradients in reasonably equilibrated films are likely to be small. If the density of initial film is homogeneous, it is likely to stay homogeneous upon heating (this follows from the incompressibility of polymer melts). Since film preparation is known to often affect film stability, it will be essential to do this experiment for more than one system (differently prepared films are likely for be frozen into different nonequilibrium morphologies, see for example the contribution by H. Richardson et al. [34]).

All in all, it will be important to do use several independent approaches (as proposed in the paper) to identify the acoustic Casimir effect. Each of the experiments may be explicable in terms of other models, but the combination of several experiments that rely on differing properties of the confinement of thermal modes should make a convincing story.