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# Post-Tanner stages of droplet spreading: the energy balance approach revisited

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## Abstract

The spreading of a circular liquid drop on a solid substrate can be described in terms of the time evolution of its base radius  $R(t)$ . In complete wetting, the quasistationary regime (far away from initial and final transients) typically obeys the so-called Tanner law, with  $R \sim t^{\alpha_T}$ ,  $\alpha_T = 1/10$ . Late-time spreading may differ significantly from the Tanner law: in some cases the drop does not thin down to a molecular film and instead reaches an equilibrium pancake-like shape; in other situations, as revealed by recent experiments with spontaneously spreading nematic crystals, the growth of the base radius accelerates after the Tanner stage. Here we demonstrate that these two seemingly conflicting trends can be reconciled within a suitably revisited energy balance approach, by taking into account the line tension contribution to the driving force of spreading: a positive line tension is responsible for the formation of pancake-like structures, whereas a negative line tension tends to lengthen the contact line and induces an accelerated spreading (a transition to a faster power law for  $R(t)$  than in the Tanner stage).

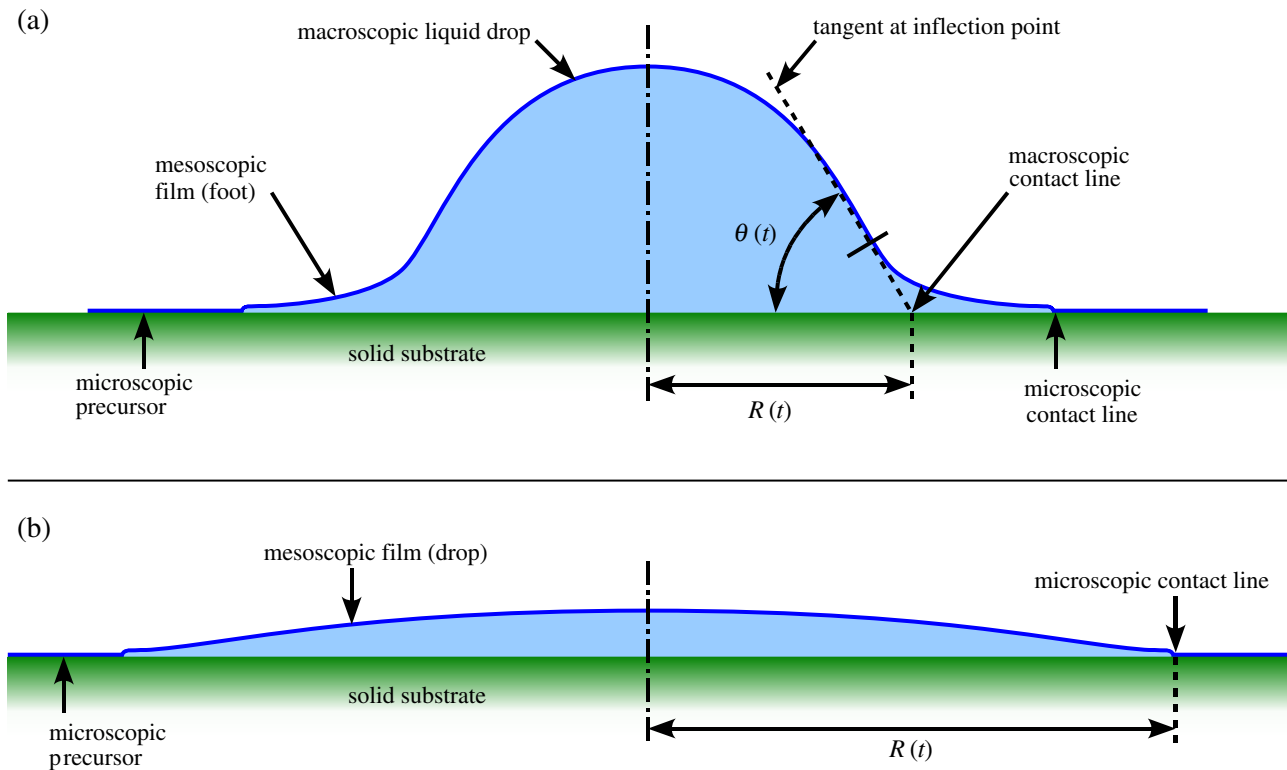
## 1. Introduction

The spreading of a liquid on a solid surface is a complicated process where many factors come into play, not necessarily known and not always controllable: the kinetic behavior may be strongly influenced or even dominated by the volatility and viscosity of the liquid (or by other rheological parameters if the liquid is non-Newtonian), by the presence of impurities in the bulk phases (chemical contaminants, surfactants, polymers, etc), by the roughness or texture of the surface, or by its crystalline structure and chemical composition. In consequence, the spreading of thin films is generally dependent upon the details of the structures and interactions in the coexisting phases. In contrast, for thicker films and drops one expects a less specific behavior, described by universal laws. However, although the prominent features of the spreading of macroscopic drops are relatively well understood [1–3], a comprehensive theoretical framework in which all of the experimentally observed phenomena harmoniously find their place is still lacking at present.

Here we are concerned with a standard textbook problem—the spontaneous spreading of a non-volatile drop on an ideal, flat, clean, horizontal, homogeneous solid surface (see figure 1). The drop has a macroscopic size but is sufficiently small that we can completely discard the effects of gravity. The spreading parameter  $S = \sigma_{SG} - \sigma_{SL} - \sigma$  is positive, so the drop tends to cover as much of the solid surface as possible to shield it against the gas phase;  $\sigma_{SG}$ ,  $\sigma_{SL}$  and  $\sigma$  are the interfacial tensions of the solid/gas, solid/liquid and liquid/gas interfaces, respectively.

We focus on the following three known features of spontaneous spreading:

- The base radius  $R(t)$  of a circular drop grows during spreading and, at intermediate times  $t$  (far from initial and final transients), typically obeys a power law  $R(t) \sim t^{\alpha_T}$  with  $\alpha_T = 1/10$  [4, 5], known as the Tanner law.
- The final stage of spreading of non-volatile droplets is not always a molecular film. Sometimes a flat,



**Figure 1.** (a) A sketch of a macroscopic liquid droplet spreading on a solid substrate.  $R(t)$  and  $\theta(t)$  denote the base radius and the contact angle of the macroscopic part of the droplet, respectively, as inferred from the inflection point at the apparent contact line. (b) A sketch of a liquid droplet at a late spreading time, in the situation where the final stage of spreading is a mesoscopic pancake. An inflection point may still exist, but the relevant  $R(t)$  now corresponds to the limit between the microscopic and mesoscopic regions; the corresponding  $\theta(t)$  is undefined.

(This figure is in colour only in the electronic version)

bounded structure is reached instead—a so-called pancake (see [1, 6–8]).

- An acceleration of the spreading process (an apparent transition from Tanner’s power law to a faster one) has been observed for spontaneously spreading nematic liquid crystals [9, 10]. Experiments revealed an algebraic growth  $R(t) \sim t^\alpha$  with  $\alpha$  nearly twice as large as the exponent  $\alpha_T$  characterizing the Tanner law:  $\alpha = 0.2$  [9] and  $\alpha = 0.19$  [10].

At the present time, it is well understood why the radius  $R(t)$  of a spontaneously spreading circular drop grows in proportion to  $t^{1/10}$ . This law has been derived analytically [4, 5, 11] and confirmed experimentally on many accounts [5, 12–14]. The fundamental argument is that the hydrodynamics in the bulk of a drop are driven by capillary forces alone, which directly yields  $R \sim t^{1/10}$  for a self-similar bulk, in the lubrication approximation [4, 5]. Alternatively, the trend can be regarded as a competition between the hydrodynamic dissipation (primarily in the contact line region of the drop) and an unbalanced capillary force [1–3, 11]. Note that the law is rather universal—in the sense that the observed exponent 1/10 is most often independent of the precise nature of the spreading liquid—and has been observed not only for simple liquids, but also for oils, polymeric liquids, liquid metals and nematic liquid crystals. For non-Newtonian liquids some deviations

from the Tanner law can be observed, attributable to their specific rheological properties and, hence, specific features of the hydrodynamic dissipation in the bulk.

The reason why in some cases a spontaneously spreading droplet attains an equilibrium pancake-like form is also clear. Such flat pancake-like structures are sometimes more favorable energetically than molecular films: this occurs when short-range interactions promote dewetting, even though the overall situation is that of complete wetting. Theoretically, such structures have been predicted and analyzed in [1, 6, 7]. They were also observed experimentally (see, e.g., [15]). A key feature of the spreading process as it reaches a pancake shape—as a transient following the Tanner stage—is that the base radius of the drop tends to a stationary value (see figure 1(b)). It must be noted, though, that the shape of such a drop differs considerably from that of a capillary cap; the geometrical meaning of  $R(t)$  is also quite different.

As opposed to the Tanner law and the emergence of mesoscopic pancakes, the physical origin of the accelerated spreading observed in [9, 10] has yet to be clarified. Also, the latter trend is apparently in conflict with the notion that a Tanner stage must be terminated by the onset of either a molecular film or a mesoscopic pancake.

Our motivation in this paper is to identify the essential factors of the spreading kinetics that might have been disregarded so far, and thus to achieve a more complete

qualitative understanding of the standard textbook problem. We focus more specifically on the spreading dynamics that may develop after the Tanner stage and try to account for the two apparently conflicting trends, possibly by introducing new notions or mechanisms. As a first step in this direction, we perform an analysis within the classical framework of an energy balance approach [1]. This approach is known to provide a qualitative derivation of the Tanner law, capturing only a few essential features of the phenomenon, in a physically transparent fashion. As noted in [16], the energy-based equations are functionally equivalent to the standard hydrodynamic approaches used in the literature but are lighter in terms of analytical calculations and assumptions involved (as compared to, e.g., phenomenological boundary conditions, should the thickness profile be described by a differential equation).

Within this approach, the Tanner law is obtained by balancing the rate of energy dissipation in the spreading macroscopic droplet and the driving force of spreading, which is taken equal to the unbalanced Young force. We point out that the analysis of de Gennes [1] disregards the line tension contribution to the driving force of spreading [17, 18]. Typically, the line tension  $\tau$  is very small—only  $10^{-10}$ – $10^{-11}$  N (see, e.g., [19–21])—and it is legitimate to neglect it when dealing with large, essentially capillary droplets. Nonetheless we show that, when such a contribution is taken into account, a consistent, non-conflicting picture emerges, with the following trends for a drop (supposedly well approximated by a spherical cap):

- At sufficiently early spreading times the effect of  $\tau$  is negligible and the Tanner stage holds.
- At long times and for negative values of  $\tau$ , the spreading process crosses over to a significantly faster power law than Tanner’s  $R \sim t^{1/10}$  (as observed for the nematic droplets [9, 10]).
- At long times and for positive values of  $\tau$ , the growth of  $R(t)$  slows down and terminates at a finite value  $R(\infty)$ . This latter trend is indicative of the emergence of pancakes.

Therefore, the approach presented in this paper resolves a seemingly controversial behavior of spreading processes, provided that a properly defined line tension  $\tau$  is taken into account. We note, however, that this approach is justified only in the case of macroscopic drops for which both the surface tension and the line tension are valid notions.

The paper is outlined as follows. In section 2 we first present the derivation of the Tanner law in terms of the energy balance approach. Then, in section 3, we revisit the standard picture by analyzing different factors which may influence the spreading kinetics, especially the notion of line tension. Finally, in section 4 we discuss possible limitations of our approach.

## 2. The energy balance approach

To lay the basis of our analysis, we start with the derivation of the Tanner law within the framework of the energy balance

approach, presented originally by de Gennes in his 1985 review paper [1]. Additional details, discussions and applications of this approach can be found in [14, 16]. Further on, in section 3, we will discuss a couple of additional factors which are missing from the seminal approach, but may account for the abnormal spreading behavior observed after the Tanner stage.

In figure 1(a) we sketched a typical configuration for a macroscopic liquid droplet spreading spontaneously on a solid substrate. The drop can be ‘divided’ into the following three regions: a ‘macroscopic’ bulk, a ‘mesoscopic’ film (a region that is within the range of surface forces), and a ‘microscopic’ precursor, the thickness of which amounts to several molecular diameters. Note that figure 1 is schematic and the relative sizes of these three regions are not to scale. For brevity, we will henceforth not use the adjectives ‘macroscopic’, ‘mesoscopic’ and ‘microscopic’; we will instead refer to the three regions as the bulk droplet, the film and the precursor.

We note first that the edge of the precursor spreads well ahead of the film and the bulk droplet: the radius of the precursor grows as  $\sqrt{t}$  [22–28] and the film plays the role of a reservoir feeding the precursor; this picture is valid as long as the said reservoir is far from being exhausted. Thus the precursor is decoupled from the rest of the drop and its only role in the process can be seen as lubricating the substrate for spreading of the film and the bulk drop.

A fundamental assumption of this approach is that the length scales of the bulk and the film are well separated, i.e., that the bulk of the drop is much wider and taller than the film. Thus the bulk can be adequately approximated by a spherical cap with the base radius  $R(t)$ , contact angle  $\theta(t)$ , and nearly constant volume  $V$  ( $V = \frac{\pi}{4}R^3\theta$  for sufficiently small  $\theta$ ), i.e., the bulk is in equilibrium at constant volume  $V$  and an instantaneous base radius  $R(t)$ .

Then, we can define an instantaneous free energy  $2\pi R(t)F(t)$  along with an instantaneous rate of energy dissipation  $2\pi R(t)W(t)$ , and propose that the evolution of these two quantities obeys the standard relationship of the mechanics of dissipative systems:

$$(W_{\text{macro}} + W_{\text{meso}} + W_{\text{micro}})R = -U \frac{d(RF)}{dR}, \quad (1)$$

where  $U = dR/dt$  is the instantaneous velocity of the apparent contact line. The right-hand side (rhs) of (1) is the rate of change of the free energy of the system. It is equivalent to the power of the driving force  $dF/dR$  applied to the moving contact line, and is balanced by the total dissipation that occurs in the system, i.e., the left-hand side (lhs) of (1). The terms  $W_{\text{macro}}$ ,  $W_{\text{meso}}$  and  $W_{\text{micro}}$  are the dissipation rates in the bulk, film and precursor, respectively, divided by the length  $2\pi R$  of the apparent contact line. Keep in mind that  $F(t)$ ,  $W(t)$  and the driving force  $dF/dR$  are also, by definition, reduced by the length  $2\pi R(t)$ .

Next we specify the rhs of (1) [1]:

$$-\frac{1}{R} \frac{d(RF)}{dR} \simeq S + \sigma(1 - \cos\theta). \quad (2)$$

Equation (2) takes into account the surface energies of the three interfaces meeting at the macroscopic contact line and

determines their variation with respect to  $R(t)$  at constant spherical cap volume. Note that the result is equivalent to a straightforward application of the Young law; in fact, the rhs of (2) is typically referred to as an ‘unbalanced Young force’.

As for the lhs of (2), we can formally decompose the dissipation according to the regions outlined in figure 1(a), as follows:  $W_{\text{macro}}$  corresponds to hydrodynamic dissipation in the bulk drop, where viscous flows are driven by the capillary pressure;  $W_{\text{meso}}$  corresponds to hydrodynamic dissipation in the film, where viscous flows are driven by the disjoining pressure;  $W_{\text{micro}}$  corresponds to friction at the microscopic scale, both at the edge of the film and in the molecular precursor.

The dissipation in the bulk drop is well approximated by that in a wedge, and is of the form

$$W_{\text{macro}} \simeq 3\eta U^2 g(\theta) \ln \left| \frac{x_{\text{max}}}{x_{\text{min}}} \right|, \quad (3)$$

where  $\eta$  is the viscosity,  $x_{\text{max}}$  and  $x_{\text{min}}$  are effective cutoff lengths for the integration over the droplet height and  $g(\theta)$  is a known function of the instantaneous contact angle. A salient feature is that the leading asymptotic behavior of  $g(\theta)$  when  $\theta \rightarrow 0$  is  $g(\theta) \simeq 1/\theta$ , which means that  $W_{\text{macro}}$  exhibits an unbounded growth as  $\theta \rightarrow 0$ . In the following we shall use the notation  $\kappa = 3 \ln \left| \frac{x_{\text{max}}}{x_{\text{min}}} \right|$ ; this is a slowly varying, empirical quantity, which varies only slightly as the droplet spreads and introduces minor, logarithmic corrections to the power laws; experimental data suggest that a good choice is a nearly constant  $\kappa \approx 120$  [13].

We now come to the dissipation in the film. A striking result of Hervet and de Gennes [11] is that the complete wetting regime is characterized by

$$W_{\text{meso}} \simeq SU, \quad (4)$$

which means that the dissipation within the film compensates exactly the first term on the rhs of (2), rendering the rate of spreading independent of  $S$ . This result was obtained for non-retarded van der Waals substrate forces, but can be generalized.

Finally, the form of the dissipation term  $W_{\text{micro}}$  was discussed by Blake and Haynes [29, 30]: it was found that  $W_{\text{micro}} \sim \zeta U^2$  at leading order in  $U$ , where  $\zeta$  is a constant friction coefficient. Note that in the case of complete wetting,  $\zeta$  is dependent on the thickness of the precursor.

Thus, provided that  $S$  is consumed entirely in the film, the dynamical behavior results from a competition between the two remaining dissipation channels,  $W_{\text{macro}}$  and  $W_{\text{micro}}$ . As  $\theta \rightarrow 0$ ,  $W_{\text{micro}}$  is independent of  $\theta$ , whereas  $W_{\text{macro}} \sim 1/\theta$  and thus clearly dominates at long spreading times. Dissipation at the microscopic contact line may dominate (e.g., for low viscosity fluids) at intermediate times, but ultimately hydrodynamic dissipation in the core drop will take over [1, 14].

Consequently, neglecting  $W_{\text{micro}}$  as compared to  $W_{\text{macro}}$ , one finds in the limit of small  $\theta$  that (1) adopts the following form:

$$\theta^3 \approx 2\kappa Ca, \quad (5)$$

which is a fundamental relation between the velocity of the moving contact line and the instantaneous value of the contact angle ( $Ca = \eta U/\sigma$  is known as the capillary number). It was derived analytically by Voinov [4] and by Tanner [5] using a different approach (within the lubrication approximation).

Now taking into account that the volume  $V \approx \frac{\pi}{4} R^3 \theta$  of the bulk drop remains nearly constant during spreading, we obtain

$$\dot{R} = \frac{64}{\pi^3} V^3 \left( \frac{\kappa \eta}{2\sigma} \right)^{-1} R^{-9}, \quad (6)$$

from which the Tanner laws  $R \sim t^{1/10}$  and  $\theta \sim t^{-3/10}$  ensue trivially. The behavior described by (5) and (6) has been observed experimentally in [5, 12, 13].

### 3. The energy balance approach revisited

Equations (2), (5) and (6), under the assumption of well separated length scales of the bulk and film, predict an unbounded growth of  $R$ . This is an ideal spreading behavior, through which the droplet virtually thins down to a molecular film. As we have already remarked, this is not always the case, as the spreading may terminate with the appearance of equilibrium pancake-like structures [1, 6, 7]. In the latter situation, the Tanner law clearly describes an intermediate stage, and the transition to a pancake must be described by some kind of crossover in terms of  $R(t)$ : our intuition is that  $R$  will tend to a finite value, although it is not clear whether the definition of  $R$  will remain consistent with figure 1(a).

An opposite trend was revealed by recent experimental studies focusing on the spontaneous spreading of nematic liquid crystals (cyanobiphenyl 5CB) on hydrophilic [9] or hydrophobic [10] substrates: after a transient Tanner stage, an ‘acceleration’ of the spreading process has been observed. The data suggest that the base radius  $R$ , as inferred from the inflection point of the thickness profile, grows algebraically but with an exponent which is substantially larger than  $\alpha_T = 0.1$ . In [9] it was shown that the Tanner law crosses over to  $R \sim t^\alpha$  with  $\alpha \approx 0.2$ . Later it was realized (see figure 6 in [10]) that the Tanner relation in (5) does not hold for late stages of spreading: for small  $\theta$  and  $Ca$  the best fit to the experimental data follows  $\theta \sim Ca^{0.7}$  rather than the form predicted by (5). The latter relation, together with the volume conservation condition  $R^3 \theta \sim V$  yields  $R \sim t^\alpha$  with  $\alpha \approx 0.19$ . A more thorough analysis of the behavior depicted in figure 5 in [10] suggests that actually the reported law  $R \sim t^{1/5}$  is only a part of a crossover from the Tanner stage to an even faster growth law. Experimental data in [10] span timescales ranging from a second to two hours, and at the end of the experiment the trend is clearly rather  $R \sim t^{1/3}$  than  $t^{1/5}$ , and possibly still accelerating. Consequently, although there is no conclusive evidence on the precise value of the exponent  $\alpha$  characterizing the accelerated spreading regime, it is clear that  $\alpha$  is significantly larger than the Tanner exponent and thus the physical mechanism responsible for the late, post-Tanner stages of spreading might be different from the one described in section 2.

### 3.1. First guess: shear thinning

We notice first that the accelerated spreading was observed for nematic liquid crystals. Nematic crystals are known to have a non-Newtonian, shear-thinning rheology (see, e.g., [31, 32]). Shear thinning affects the flow pattern, which necessarily modifies the spreading dynamics. Thus our first idea is to revisit the lhs of (1) and, more specifically, the term  $W_{\text{macro}}$  in (3). The expression (4) for  $W_{\text{meso}}$  is also queried in the case of shear thinning.

A detailed analysis of the contact line dynamics within the framework of the thin film model shows that the characteristic shear rates in the capillary wedge and in the film decrease as the contact line velocity decreases [33]. In consequence, for a spontaneously spreading droplet of a non-Newtonian, shear-thinning fluid the effective viscosity will increase with time, resulting in a spreading law of the form  $R \sim t^\alpha$  with  $\alpha < 1/10$ . Numerical simulations carried out in [34] confirm that  $\alpha < 1/10$  for shear-thinning fluids and that  $\alpha > 1/10$  for shear-thickening fluids. Hence the dominant effect from shear thinning is that the spontaneous spreading of a non-Newtonian fluid is generally slower than predicted by the Tanner law and cannot explain the experimentally observed acceleration of the spreading process.

### 3.2. Second guess: line tension

We now turn our attention to the rhs of (1) and notice that the unbalanced Young force—which is also the rhs of (2)—is, in fact, a mere approximation of the actual driving force of spreading. In general, the total free energy of the liquid/solid system can be decomposed into bulk, surface, line, and point contributions (see, e.g., [17, 18]). Thus, the driving force (2), as a derivative of the total free energy, should also contain all these contributions. This picture, of course, is meaningful only in the case of macroscopic drops, for which both the surface tension and the line tension are well defined.

As a matter of fact, the spherical cap adequately describes the profile of the bulk drop, but the profile of the mesoscopic film deviates from it, such that the quasistationary free energy  $2\pi RF$  must include a correction term, which is accumulated in the vicinity of the apparent contact line and can be seen as a line energy  $\tau$  multiplied by the apparent perimeter  $2\pi R$  [35]. The expression (2) takes into account the surface energies of the three macroscopic interfaces meeting at the apparent contact line, but does not include the line tension contribution.

The idea that the line tension may have an appreciable impact on the global behavior is not new. As an excess quantity,  $\tau$  can be positive or negative, as noticed already by Gibbs [36]. Negative line tension, for example, can significantly reduce the work required to create a nucleus (100 Å in diameter) of a new phase on solid or liquid substrates [37]. Conversely, positive line tension can explain the stability of Newtonian black films towards rupture [38]. For liquid droplets of nanometer size, negative (resp. positive) line tension can promote spreading (resp. dewetting) even if the macroscopic spreading parameter  $S$  is negative (resp. positive) [35]. A review of different phenomena caused

by line tension effects and some conceptual aspects of line tension can be found in [17, 18].

Evaluation of the contribution due to the line tension  $\tau$  involves many delicate issues (e.g., a proper definition of the effective interface potential used in the model, or a proper convention when choosing the Gibbs dividing interface) and, in general, is a more complex problem than the calculation of the surface tension—essentially because more phases meet at the contact line than at an interface (see, e.g., [17, 18] for a more thorough discussion). The problem is already difficult in equilibrium situations (e.g., partial wetting, with  $S < 0$ ), and clearly becomes even more complex when one considers spontaneous spreading, since here one has to account for the temporal evolution of the droplet thickness profiles.

The consideration of these subtle points is beyond the scope of the present approach. For our purposes it will be sufficient to resort to a recently proposed phenomenological generalization of (2) in terms of non-equilibrium thermodynamics: as shown in [39], the force applied to the apparent contact line of a droplet can be written down as

$$f_\tau = S + \sigma(1 - \cos\theta) - \frac{\tau}{R}, \quad (7)$$

which differs from the expression in (2) by an additional term accounting for the contribution of the contact line tension  $\tau$  to the driving force of spreading. The definition of  $f_\tau$  as a generalized Young force is valid both in complete and partial wetting, and is consistent with the so-called modified Young equation  $f_\tau = 0$ , obtained at equilibrium by an appropriate generalization of Gibbs classical theory of capillarity [35, 40].

At this point we must stress that the expression (7) for  $f_\tau$  is formally valid only if  $\tau$  is constant. If we assume a power-law behavior for  $\tau \sim R^\beta$ , then the modified Young force becomes  $S + \sigma(1 - \cos\theta) - \frac{\tau}{R}(1 + \beta)$ . Here we argue that it is not likely for  $\tau$  to vanish at long  $t$  and large  $R$ , and thus  $\beta \geq 0$ . Thereby (7) essentially holds for  $\tau \sim R^\beta$ , up to a numerical factor  $(1 + \beta) > 0$  applied to the line tension term, i.e., the last term on the rhs of (7). This consideration has little impact on the following qualitative argument, but will be relevant to quantitative implications.

### 3.3. Line tension effects on spreading

Suppose now that (1) holds; that the dissipation  $W_{\text{meso}}$  in the film obeys (4); that the dissipation  $W_{\text{macro}}$  is given by (3); but that the driving force of spreading is now determined by (7), i.e., that the line tension contribution is taken into account. Then (5) is replaced with the following:

$$\kappa \frac{\eta}{\theta} \dot{R} = \frac{1}{2} \sigma \theta^2 - \frac{\tau}{R}. \quad (8)$$

Since  $\tau$  is typically very small, one naturally finds that the surface tension contribution will dominate at small and intermediate times, again giving rise to the Tanner law  $R \sim t^{1/10}$ . On the other hand, as  $R$  grows to sufficiently high values, the line tension contribution will inevitably take over and become a dominant driving force, provided that  $\tau/R$  decays more slowly than the capillary term  $\sigma\theta^2$ .

In the latter regime, the behavior is crucially dependent on the sign of  $\tau$ :

- If  $\tau$  is positive and tends to a constant value, which is physically plausible, then (8) predicts that spreading will terminate at a finite value of  $R$ , for which the first and the second terms on the rhs of (7) become equal to each other. One may interpret this as an indication of the formation of a pancake. However, during the actual transition to a pancake, a drop would not retain the shape of a capillary cap (see figure 1(b)), which somewhat challenges this prediction.
- If  $\tau$  is negative and the second term in (8) dominates, we find the following post-Tanner behavior:

$$R \sim \left( - \int^t \tau dt \right)^{1/5}. \quad (9)$$

This spreading law is qualitatively different from  $R \sim t^{1/10}$ . In the framework outlined in section 2, the driving force of spreading is associated with the surface tension. By contrast, during the late stages of spreading, the droplet becomes flatter and can be viewed as ‘quasi-two-dimensional’. It is then not surprising that the line tension  $\tau$  should govern the spreading process, provided that  $|\tau| \gg \sigma R\theta^2$ .

It is tempting to obtain coarse quantitative results from (9) and from the condition  $|\tau| \gg \sigma R\theta^2$ . In particular, if we assume that  $\tau$  is a negative constant, then (9) predicts  $R \sim t^{1/5}$ , which agrees with previously reported experimental results [9, 10]. Looking at figure 5 in [10] we can estimate the value of  $\tau$  from the characteristic base radius at the apparent crossover between the Tanner stage and the accelerated spreading regime: this yields  $\tau \approx -10^{-9}$  N. This value is an order of magnitude higher than previously reported values of the line tension in the partial wetting situations, but it must be noted that many experimental measurements of  $\tau$  have been performed for simple liquids; in the case of nematic liquid crystals an elastic contribution to the effective interface potential (a consequence of the anchoring properties) may yield substantially higher values of  $\tau$ .

However, upon a closer examination of the case of negative  $\tau$ , there is no good reason to expect that  $\tau$  should approach a constant value. One rather expects the film region to become progressively more pronounced and the drop profile to significantly deviate from a spherical cap-like shape; hence  $\tau$ , a functional of local droplet thickness, will grow as a function of time (in terms of its absolute value). Consequently, at late spreading stages, one may expect a growth of  $R(t)$  that is faster than  $R \sim t^{1/5}$ .

#### 4. Conclusions

We have presented in this paper both the classical energy balance approach—as developed by de Gennes—and a revised version of it, which incorporates a line tension contribution to the driving force of spreading. The revisited framework was motivated by apparently contradictory trends at long spreading times for macroscopic droplets in complete wetting. By taking line tension into account, we have complemented the classical framework with the following twofold interpretation:

- A positive line tension—essentially a ‘collar’ around a spreading droplet—stops spreading and is responsible for the formation of mesoscopic pancakes.
- A negative line tension—which tends to lengthen the apparent contact line—governs the late stages of spreading, resulting in the acceleration of this process.

We must now voice a few words of caution concerning our approach, which seems intuitive but may have several shortcomings due to its simplicity.

First we admit that the formal definition of line tension  $\tau$  in partial wetting—a functional of an equilibrium profile, and an integral of the effective interface potential—cannot be easily generalized to complete wetting and thus remained undetermined within our analysis. The case of constant, positive  $\tau$  is plausible, but negative  $\tau$  is more likely to grow as a function of time and base radius, a growth which we are unable to specify. We merely expect that, as in the partial wetting case,  $\tau$  is a certain functional of the mesoscopic thickness profile, rather than an independent, arbitrary quantity (see, e.g., [41]).

We have already stated that in the case of positive  $\tau$  our prediction of the emergence of pancakes is indicative at best: indeed, in the process of reaching the stationary shape of a pancake, a droplet gradually deviates from the spherical cap shape assumed by sections 2 and 3; this deviation entails corrections that our approach does not account for. A similar word of caution exists for negative  $\tau$  and arises from a thorough comparison with experiment. Indeed, a remarkable feature of nematic 5CB droplets observed in [9, 10] is that the reported accelerating phase is accompanied by the development of a large ‘foot’ (essentially the drop adopts a bell shape similar to figure 1(a), without exaggeration). This large foot is a warning against the applicability of energy balance as developed in sections 2 and 3: the key assumption of a spherical cap of constant volume  $V_{\text{cap}} = \frac{\pi}{4} R^3 \theta$  is increasingly less valid as the mesoscopic film drains liquid from the macroscopic droplet. In other words, the separation of macroscopic and mesoscopic length scales (both vertical and lateral), in the experimental layout that we are trying to describe, may be more precarious than what was assumed in our analytical framework.

In the light of these shortcomings, our agenda is to develop a more robust approach describing late stages of droplet spreading, based on the seminal approach by Tanner describing the time evolution of the thickness profile of whole droplets within the thin film approximation [4, 5]. In the latter framework, scale separation is not an issue, and the fundamental result is that droplets gradually turn into diffusive films in the sense of Derjaguin [42]. Results have already been obtained for the specific case of nematic droplets, and we shall present them in a companion paper [43].

We are also looking forward to developing the notion of a dynamic line tension in spreading processes, through a detailed study of the hydrodynamic wedge [1, 44, 45]. It is important to note that nematic 5CB droplets exhibit both of the non-trivial types of post-Tanner behavior detailed in this paper:  $R(t)$  crosses over from  $R \sim t^{0.1}$  to faster power laws (at this point the drop looks like figure 1(a)), but eventually the spreading terminates with a mesoscopic pancake (figure 1(b)). In terms of  $\tau$ , this means that the physically relevant line tension

is negative during the accelerating phase, but later becomes positive. As figure 1 suggests, the geometrical properties of the droplet are quite different in the two regimes, and it is not clear whether a consistent definition of  $\tau$  can be established for such liquids as nematic liquid crystals.

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