The fluid dynamics of the classical dewetting instability in ultrathin films is a non-linear process. However, the physical manifestation of the instability in terms of characteristic length and time scales can be described by a linearized form of the initial conditions of the film’s dynamics. Alternately, the thermodynamic approach based on equating the rate of free energy decrease to the viscous dissipation [de Gennes, C. R. Acad. Paris. v298, 1984] can give similar information. Here we have evaluated dewetting in the presence of thermocapillary forces arising from a film-thickness (h) dependent temperature. Such a situation can be found during pulsed laser melting of ultrathin metal films where nanoscale effects lead to a local h-dependent temperature. The thermodynamic approach provides an analytical description of this thermocapillary dewetting. The results of this approach agree with those from linear theory and experimental observations provided the minimum value of viscous dissipation is equated to the rate of free energy decrease. The flow boundary condition that produces this minimum viscous dissipation is when the film-substrate tangential stress is zero. The physical implication of this finding is that the spontaneous dewetting instability follows the path of minimum rate of energy loss.

I. INTRODUCTION

Investigations of thin film morphology evolution and control is of fundamental and technological interest. In particular, spontaneous self-organizing processes [1] that lead to nanostructure formation in a reliable way have attracted tremendous attention. The resulting nanostructures can have novel behavior as well as be utilized in a wide variety of technologies, such as, energy harvesting [2–4], biomedicine [5, 6], spintronics [7], photonics [8] and magnetism [9, 10]. One example of a self-organizing process is the spontaneous dewetting of a continuous liquid film from a surface. A scientific understanding of dewetting has implications to many industrial applications, including in the deicing of airplane wings with non-wettable surfaces, in preventing hydroplaning of automobiles on wet roads due to thin continuous layer of water and in designing chemicals to prevent the break-up of the lacrimal film that protects the cornea of the eye. Another growing application of dewetting is in the fabrication of nanoscale structures in a robust, controllable and cost-effective manner. The extensive studies of polymer thin films and growing number of investigations of dewetting in metallic thin films is indicative of this technological interest and also to the need for a deeper understanding of the phenomenon [11–20].

The classical dewetting instability in thin films can be interpreted as a competition between two energy terms. For the case of a large number of polymer or metallic films studied, these two energies correspond to the surface tension and the attractive intermolecular dispersion force between the film-substrate and film-vacuum interfaces mediated by the film material. As shown first by Vrij [21, 22], the instability can be described from an energetic viewpoint by evaluating the thermodynamic free energy change of the system under perturbations to the film height. The prediction from such an energy analysis is that for certain perturbation wave vectors, the film enters an unstable state and thus, can spontaneously dewet. As a result, studies of dewetting have focused largely on the fluid dynamics of the film, through which it is possible to obtain the relationship between the rate of growth or decay of surface perturbations to their wave vector, i.e. the dispersion relation. However, the fluid dynamics for even the simplest dewetting scenario, such as the example above, is a highly nonlinear process, and, while addressable by many numerical techniques [23, 24], is often evaluated through a linear analysis in order to achieve physical insights into dewetting. An alternate approach to quantitatively evaluate dewetting is thermodynamics. Fluid flow pathways can be analyzed through thermodynamic considerations in which the conversion of useful internal energy to external energy loss via heat, such as by viscous dissipation, is used to quantify the behavior [27, 28].

In this work, we show that such an approach can provide meaningful insight into the nature of fluid flow as well as the energy pathway for dewetting instabilities. Specifically, we have applied the thermodynamic formulation to the case of dewetting in which film thickness dependent Marangoni or thermocapillary forces are also present. Such a situation has been observed in the melting of thin metallic films by nanosecond pulsed lasers [29, 30]. In our thermodynamic analysis the rate of thermodynamic free energy decrease due to film thickness fluctuations is balanced with the rate of energy loss due to viscous flow, i.e. viscous dissipation. This leads to a analytical description of the dewetting process without explicit need to solve the the height evolution dynamical equation from the Navier-Stokes (NS) equation. The thermodynamic and linear approach show identical results for classical dewetting. For thermocapillary dewetting, the two approaches agree only if the minimum viscous dissipation is evaluated. This minimum was found to occur for a particular flow boundary condition, which related the pressure gradient with the thermocapillary forces, and resulted in zero tangential stress at the film-substrate interface. Besides this physical insight into the fluid flow, the thermodynamic analysis also showed that the dewetting pathway is one in which the rate of energy loss is...
minimized.

II. THEORY

For completeness, we first begin by summarizing the derivation of the thin film fluid velocity for a one-dimensional (1D) incompressible fluid from the NS equation within the lubrication approximation. A complete analysis is provided in ref. [31]. In this approximation the average or unperturbed thickness \( h_0 \) of the film is much smaller than the in-plane dimension (x), as a result of which, the only velocity change of importance occurs along the thickness or z-direction. Furthermore, because of the small thickness of the film, inertial effects can be neglected and so the flow is dominated by the viscous effects. Using the above approximations, the NS equation for the steady-state condition (\( \rho \frac{dv}{dt} = 0 \)) in the x-direction is given by:

\[
\nabla P = \eta \frac{d^2 v}{dz^2}
\]

where \( v \) is the x-component of the liquid velocity, \( \nabla P = \frac{dp}{dx} \) is the pressure gradient in the direction of flow x, and \( \eta \) is the dynamic viscosity. By integrating the velocity \( v \) as a function of height \( z \) we get:

\[
v = \nabla P z^2 + az + b
\]

Typical boundary conditions used to analyze the classical dewetting instability are the no-slip condition at the film-substrate, so \( v(h = 0) = 0 \), and a stress-free boundary condition at the top film surface. The no-slip condition results in \( b = 0 \). At the top surface, we introduce the h-dependent Marangoni effect by equating the shear stress to the surface tension gradient:

\[
\eta \frac{dv}{dz} \bigg|_{h_0} = \frac{d\gamma}{dh} \frac{dh}{dx} = \gamma_h' h_o, \quad \text{where, } \gamma_h = \frac{d\gamma}{dh} \frac{dh}{dx}
\]

and

\[
\frac{dh}{dx} = h'
\]

From this, the velocity and velocity gradient in the z-direction can be respectively expressed as:

\[
v = \nabla P z^2 - \frac{\nabla Ph_0 - \gamma h'}{\eta} z
\]

and

\[
\frac{dv}{dz} = \frac{\nabla P}{\eta} z - \frac{\nabla Ph_0 - \gamma h'}{\eta}
\]

Based on this, one can now easily evaluate the rate of energy loss due to viscous liquid flow, i.e. the viscous dissipation, per unit volume \( \dot{e} \) occurring in the film. This quantity is given by [32]:

\[
\dot{e} = \eta (\frac{dv}{dz})^2 = \frac{(\nabla P)^2 z^2}{\eta} - 2\nabla P (\nabla Ph_0 - \gamma h') z + \frac{(\nabla Ph_0 - \gamma h')^2}{\eta}
\]

For the case of classical dewetting, i.e. in which Marangoni forces are absent (\( \gamma_h = 0 \)), the viscous dissipation will be:

\[
\dot{e}_C = \frac{(\nabla P)^2}{\eta} (z - h_0)^2
\]

where the superscript denotes classical.

Next, we can evaluate the rate of thermodynamic free energy change \( \Delta F \) for fluctuations/perturbations to the initial height of the film. Since we are primarily concerned with the dewetting instability, we will use the classical approach proposed by Vrij where-in the film-vapor surface tension energy competes with the attractive dispersion energy. Film height perturbations will increase the top film surface area and so surface tension increases the overall thermodynamic free energy of the film. On the other hand, the long range attractive dispersion energy varies as \( \Pi'' = A/2r^4 \), where A is the Hamaker coefficient with negative sign, leading to an overall decrease in thermodynamic free energy. As Vrij showed, it is the free energy decrease resulting from competition between these two energy terms that drives the dewetting instability. Here, we evaluate the rate of this free energy change by expressing the height perturbations as Fourier components of type:

\[
h(x,t) = h_0 + \varepsilon e^{\sigma t} e^{-ikx}
\]
where the perturbation has an amplitude of \( \varepsilon \), a characteristic temporal decay rate \( \sigma \) and a corresponding wave vector \( k \). In this work, we explore the thermodynamic solution for a thermocapillary/Marangoni problem where the surface tension is dependent on the local height but independent of the \( x \)-position on the surface. Consequently, the surface tension change does not contribute to a change in free energy. This can be shown as follows. The standard procedure is to calculate the rate of total free energy change due to the height perturbation and evaluate it over one wavelength of the perturbation \[21\]. In this case, the resulting rate of energy change will be

\[
\Delta F_{\text{single wavelength}} = \int_0^L \left( \frac{1}{2} \gamma | \frac{\partial h}{\partial x} |^2 + \frac{1}{2} \Pi'' \Delta h^2 + \frac{1}{2} \gamma \Delta h \right) dx
\]  

(8)

One can immediately see that when the magnitude of the surface tension derivative with respect to height \( (\gamma_h = d \gamma/dh) \) is independent of the \( x \)-position along the film, the integral of the third term is \[ \int_0^L \frac{1}{2} \Pi'' \gamma_i e^{-ikx + \sigma t} dx = 0 \]. Consequently, to calculate the rate of change in the free energy, we can ignore the contribution from \( \gamma_h \) and express it as the difference due to the initial and perturbed film thickness at any position \( x \) \[22\] as:

\[
\Delta F = \frac{\partial}{\partial t} \left( \frac{1}{2} \gamma \left| \frac{\partial h}{\partial x} \right|^2 + \frac{1}{2} \Pi'' \Delta h^2 \right) = \sigma (\gamma k^2 + \frac{A}{2\pi h_0}) \varepsilon^2 e^{2(\sigma t - ikx)}
\]

(9)

The first term in the expression on the right hand side is the rate of increase of surface tension energy, and the second one is the rate of change in energy from the dispersive interaction.

### III. RESULTS

#### A. Dispersion relation for classical dewetting

Here we compare the characteristic dewetting length scales obtained from fluid dynamics versus the thermodynamic approach. The typical approach to obtain the dispersion relation between the rate \( \sigma \) and wave vector \( k \) has been to describe the rate of change in film height based on the NS equation and mass conservation \[21,22\]. For the classical dewetting instability, i.e. without Marangoni effects, the resulting dynamics is described by the equation \[18,53\]:

\[
3\eta \frac{\partial h}{\partial t} = -\nabla \cdot \left( \gamma h^3 \nabla \cdot \nabla h - \frac{A}{2\pi h} \nabla h \right)
\]

(10)

As is evident, this equation is non-linear in \( h \) and presents considerable challenges towards achieving an analytical description of dewetting that could provide simple but physically insightful information about the instability. Consequently, a prevalent approach is a solution afforded by linear stability analysis. Hence, after an expansion of the right hand side of Eq. \[10\]

\[
3\eta \frac{\partial h}{\partial t} = (-k^2 \varepsilon e^{\sigma t - ikx}) \left( \gamma k^2 h_0^3 + 6h_0^2 \varepsilon e^{\sigma t - ikx} + 9h_0 \varepsilon e^{2(\sigma t - ikx)} + 4\varepsilon^3 e^{3(\sigma t - ikx)} + \frac{Ah_0}{2\pi(h_0 + \varepsilon e^{\sigma t - ikx})^2} \right)
\]

(11)

and applying by keeping terms only linear in the perturbation amplitude \( \varepsilon \), as required by LSA, Eq. \[11\] reduces to :

\[
3\eta (\varepsilon \sigma e^{\sigma t - ikx}) = (-k^2 \varepsilon e^{\sigma t - ikx}) \left( \gamma k^2 h_0^3 + \frac{A}{2\pi h_0} \right)
\]

(12)

Consequently, the resulting dispersion relation is given by \[29\]:

\[
\sigma_{\text{LSA}}^2 = \frac{k^3 h_0^2}{3\eta} (\gamma k^2 + \frac{A}{2\pi h_0})
\]

(13)

The characteristic (or classical) dewetting length scale \( \Lambda_{\text{LSA}} \) can be obtained from the dispersion relation by the maxima condition \( \frac{d\sigma}{dk} = 0 \) and leads to:

\[
\Lambda_{\text{LSA}} = \left( -\frac{8\pi^2 \gamma h_0^3}{A} \right)^{1/2} = \sqrt{-\frac{16\pi^2 \gamma h_0^2}{A}}
\]

(14)
where the superscript refers to LSA.

On the other hand, the thermodynamic (TH) approach is based on equating the rate of free energy change (Eq. 9) to the total viscous dissipation in the film. We can calculate the total viscous dissipation per unit area \( \dot{E} \) for the liquid film by integrating over the film thickness as follows:

\[
\dot{E}_C = \int_0^{h_0} \dot{e}_C dz = \frac{(\nabla P)^2}{3\eta} h_0^3
\]

(15)

The next, and important, step in evaluating this integral is to relate the pressure gradient to the film height through a volume conservation argument. Volume conservation requires that the rate of change of film height \( \frac{\partial h}{\partial t} \) be related to the flux of liquid flow \( J(x) \) as \( \frac{\partial h}{\partial t} = -\nabla \cdot J(x) \). To evaluate this we have used the thin film lubrication approximation in which flux can be written in terms of the height-averaged liquid velocity \( \bar{v} \) as [31]:

\[
J(x) = h_o \bar{v} = h_o \left( \frac{1}{h_o} \int_0^{h_o} v dz \right) = -\frac{\nabla P}{3\eta} h_o^3
\]

(16)

from which we can express the volume conservation equation as:

\[
\frac{\partial h}{\partial t} = -\nabla \cdot J = \frac{\nabla^2 P}{3\eta} h_o^3
\]

(17)

By rearranging terms we get the desired relation for the pressure gradient as follows:

\[
\nabla P = \int \nabla^2 P dx = \frac{i}{k} \left( \frac{3\eta \sigma}{h_o^3} \right) e^{i\sigma t - ikx}
\]

(18)

where we have made use of Eq. 7. Using this expression in Eq. 15, the total dissipation is:

\[
\dot{E}_C = -\frac{3\eta}{h_o^3} \sigma^2 e^{2(i\sigma t - ikx)}
\]

(19)

Then, equating Eq. 19 with the rate of decrease of free energy, Eq. 9 \( \Delta F = \dot{E}_C \), and expressing the result in terms of \( \sigma \) we get the dispersion relation from the thermodynamic approach:

\[
\sigma_{TH} = -\frac{h_o^3 k^2}{3\eta} (\gamma/\sigma + A/2\pi h_o^4)
\]

(20)

from which, the classical dewetting length scale \( \Lambda_{TH} \) can be expressed as:

\[
\Lambda_{TH} = \left( -\frac{8\pi^2 \gamma h_o^3}{A \frac{\pi^2}{2\pi h_o^4}} \right)^{1/2} = \sqrt{\frac{16\pi^2 \gamma}{A h_o^2}}
\]

(21)

where the superscript and subscript refers to thermodynamic. As expected, the fluid dynamics described by LSA and the TH approach give identical results for the classical dewetting instability [27, 34]. On the other hand, as we show next, dewetting with Marangoni (or Thermocapillary) forces requires a more stringent evaluation of the viscous dissipation in order to provide results comparable to LSA.

**B. Dispersion relation for thermocapillary dewetting from thermodynamics**

As in the previous section, we analyze the LSA and TH approaches for dewetting in the presence of thickness-dependent Marangoni effects. In order to relate our work to experimental observations, we describe LSA results for the case when ultrathin metal films on SiO\(_2\) substrates are melted by nanosecond ultraviolet wavelength laser pulses [14, 17]. In this situation, there is a strong thickness-dependent reflection and absorption of light by the thin metal film which leads to a local \( h \)-dependent temperature of the liquid metal film [19]. In addition, as reported previously, the temperature gradient along the plane of the film, \( dT/dx \), generated by this nanoscale heating effect, can have a positive or negative sign depending upon the initial film
thickness $h_o$ \[^{[29]}\]. With this, the boundary condition describing the $h$-dependent Marangoni effect can be rewritten in the form of a thermocapillary effect as follows:

$$
\eta \frac{dv}{dz} \bigg|_{h_o} = \frac{d\gamma(h)}{dh} \frac{dh}{dx} = - | \gamma_T | T_h h' \tag{22}
$$

Where $\gamma_T = \frac{d\gamma}{dT}$ is the temperature coefficient of surface tension, $T_h = dT/dh$ is the film height-dependent temperature and $h' = dh/dx$. Given that all metals have a negative value of $\gamma_T$, we have expressed the boundary condition in a more conventional form using $\gamma_T = - | \gamma_T |$. In this scenario, the resulting dynamical equation of the film height is given by:

$$
3\eta \frac{\partial h}{\partial t} = - \nabla \cdot \left( \gamma h^3 \nabla h - \frac{A}{2\pi h} \nabla h + \frac{3}{2} h^2 \nabla \gamma \right) \tag{23}
$$

Applying steps similar to the classical case, the right hand side of Eq. \[^{[23]}\] is:

$$
3\eta \frac{\partial h}{\partial t} = -(\epsilon e^{\sigma_T - ikx}) \left( \gamma k^4 (h_o + \epsilon e^{\sigma_T - ikx})^2 \left( h_o + 4\epsilon e^{\sigma_T - ikx} \right) + \frac{A(k^2 h_o)}{2\pi (h_o + \epsilon e^{\sigma_T - ikx})^2} + 3k^2 | \gamma_T | T_h (h_o + \epsilon e^{\sigma_T - ikx}) \left( \frac{h_o}{2} + \frac{3}{2} \epsilon e^{\sigma_T - ikx} \right) \right) \tag{24}
$$

which, upon applying LSA, reduces to:

$$
3\eta (\epsilon e^{\sigma_T - ikx}) = -(\epsilon e^{\sigma_T - ikx}) \left( \gamma k^4 h_o^3 + \frac{A k^2}{2\pi h_o} + \frac{3}{2} \frac{| \gamma_T |}{| T_h |} \right) \tag{25}
$$

and the resulting dispersion relation is\[^{[29]}\]:

$$
\sigma^L_{TC} = -\frac{h_o^3 k^2}{3\eta} \left( \gamma k^4 + \frac{A}{2\pi h_o^4} \right) + \frac{3}{2} \frac{| \gamma_T |}{| T_h |} \tag{26}
$$

From Eq. \[^{[26]}\] the characteristic dewetting length scale in the presence of thermocapillary effects, $\Lambda^L_{TC}$, can be expressed as:

$$
\Lambda^L_{TC} = \frac{2\pi}{k} \left( -\frac{16\pi^3 \gamma}{A + 3\pi | \gamma_T | h_o^3 T_h} \right)^{1/2} \tag{27}
$$

where the superscript $TC$ denotes thermocapillary.

Next we evaluate the length scale using the TH approach based on evaluating the total viscous dissipation per unit area $\dot{E}$ for the liquid film. First, the dissipation per unit volume expressed in terms of the thermocapillary boundary condition is:

$$
\dot{E}_{TC} = \eta \left( \frac{dv}{dz} \right)^2 = \frac{\nabla P^2}{\eta} (z - h_o)^2 - 2\nabla P \frac{| \gamma_T | T_h h'}{\eta} (z - h_o) + \frac{(| \gamma_T | T_h h')^2}{\eta} \tag{28}
$$

The total viscous dissipation per unit area $\dot{E}$ for the liquid film is now:

$$
\dot{E}_{TC} = \int_0^{h_o} \dot{E}_{TC} dz = \frac{\nabla P^2}{3\eta} h_o^3 + \nabla P \frac{| \gamma_T | T_h h'}{\eta} h_o^2 + \frac{(| \gamma_T | T_h h')^2}{\eta} h_o \tag{29}
$$

Again, the next step in evaluating this integral is to relate the pressure gradient to the film height through volume conservation arguments, as done for the classical case.

$$
J(x) = h_o < v > = h_o \left( \frac{1}{h_o} \int_0^{h_o} vdz \right) = - \frac{\nabla P}{3\eta} h_o^3 - \frac{| \gamma_T | T_h h'}{2\eta} \tag{30}
$$

from which we can express the volume conservation equation as:

$$
\frac{\partial h}{\partial t} = - \nabla J = \frac{\nabla^2 P}{3\eta} h_o^3 + \frac{| \gamma_T | T_h h'}{2\eta} \tag{31}
$$
By rearranging terms and substituting the height perturbation, Eq. 7 into above we get:

\[ \nabla^2 P = \frac{3\eta}{h_0^3} e^{\sigma t - ikx} + \frac{3}{2h_0} |\gamma r| T_h k^2 e^{\sigma t - ikx} \]  

(32)

The pressure gradient along the x-direction can now be obtained by integrating Eq. 32 as follows:

\[ \nabla P = \int \nabla^2 P dx = i \left( \frac{3\eta \sigma}{h_0^3} + \frac{3}{2h_0} |\gamma r| T_h k^2 \right) e^{\sigma t - ikx} \]  

(33)

Then, on substituting the above relation for pressure gradient into Eq. 29 we get the total viscous dissipation:

\[ E_{TC} = \left\{ -\left( \frac{3\eta h_0^3 k^2}{\sigma} + \frac{3}{4\eta} |\gamma r| T_h \right) + \frac{3}{2h_0} \frac{h_0^3}{\eta} \right\} e^{\sigma t - ikx} \]  

(34)

Finally, equating Eq. 34 with the rate of decrease of free energy, Eq. 9 and rearranging the equation in terms of \( \sigma \) we get an analytical dispersion expression for thermocapillary dewetting as:

\[ \sigma^2 + \frac{h_0^3 k^2}{3\eta} (\gamma k^2 + \frac{A}{2\pi h_0^2}) \sigma + \frac{h_0^3 k^2}{3\eta} (\frac{\gamma r|T_h|^2k^2 h_0}{4\eta}) = 0 \]  

(35)

It is important to note that Eq. 35 which comes from the thermodynamic approach, differs from the LSA result, Eq. 26. One can note that there is substantial difference between the two solutions. The TH approach is quadratic in \( \sigma \) as well as \( |\gamma r| T_h \) (Eq. 35), while, in the LSA case (Eq. 26) it is linear in both quantities. Consequently, the TH approach does not directly lead to the linear dependence on \( |\gamma r| T_h \) as evident from LSA (Eq. 26). This is especially important since, as noted earlier, the thermal gradients generated by pulsed laser heating can have positive or negative signs and hence lead to fundamentally different dewetting behaviors [29, 30]. Since the TH dispersion is a quadratic function of the thermal gradient, its behavior will be independent of the sign of the thermal gradient and so does not agree with LSA. As we show next, it is necessary to evaluate the characteristics of dissipation in order to get the correct behavior from TH.

1. Dispersion using minimum viscous dissipation

In the classical case, the total viscous dissipation is uniquely defined by the magnitude of the pressure gradient for any given film thickness, as evident from Eq. 15. On the other hand, the total dissipation for thermocapillary dewetting is not unique, and, in fact, varies with the magnitude of the thermal gradient for any given pressure gradient, as evident from Eq. 29. It is this behavior that is responsible for the above discrepancy between LSA and TH and can be resolved by evaluating the minimum viscous dissipation.

The minimum viscous dissipation for the fluid being subjected to pressure gradients can be estimated from the differential condition \( d\dot{e}/d\nabla P = 0 \). Using Eq. 28 this leads to the condition \( \nabla P (z - h_0) = |\gamma r| T_h' \). The general solutions satisfying the above equality can be evaluated for various values of height \( z \) in relation to the thickness \( h_0 \). First, the condition \( z = h_0 \) does not yield a unique relation between \( \nabla P \) and \( \gamma h' \) and is therefore not a useful solution in the context of the dissipation. On the other hand, the choice of \( z = 0 \), yields the case of \( \nabla P = -|\gamma r| T_h' / h_0 \). By utilizing Eq. 28 one can see that the physical interpretation of this condition is that the tangential stress at the film-substrate interface at \( z = 0 \) is zero. The resulting viscous dissipation for thermocapillary dewetting will now be (from Eq. 28):

\[ \dot{e}_{TC}^m = \frac{(\nabla P z)^2}{\eta} \]  

(36)

where the superscript \( m \) signifies a minimum. One can verify that this is a minima by noting that the second derivative \( d^2\dot{e}_t/d\nabla P \) is positive. Therefore, the minimum dissipation per unit area of the film \( \dot{E}_{TC}^m \) can be obtained as:

\[ \dot{E}_{TC}^m = \int_0^{h_0} \dot{e}_{TC}^m dz = \frac{(\nabla P)^2 h_0^3}{3\eta} \]  

(37)
Using the form of $\nabla P$ from Eq. 33, the relevant form of $\dot{E}_{TC}^m$ is:

$$\dot{E}_{TC}^m = -\left( \frac{3\eta}{h_0^3 k^2} \sigma^2 + \frac{3}{h_0} \left| \gamma_T \right| \sigma + \frac{3}{4\eta} \left( \gamma_T \right)^2 h_0^2 \right) e^2(\sigma-i\kappa)$$

(38)

Finally, by equating the rate of free energy change $\Delta F$ (Eq. 9) and the minimum viscous dissipation rate $\dot{E}_{TC}^m$, (Eq. 38), we obtain an analytical form of the dispersion relation as:

$$\sigma^2 + \frac{h_0^3 k^2}{3\eta} (\gamma_T^2 + \frac{A}{2\pi h_0^2}) + \frac{3}{\eta} \left| \gamma_T \right| \sigma + \frac{h_0^3 k^2}{3\eta} \frac{3}{4\eta} \left( \gamma_T \right)^2 h_0^2 k^2 = 0$$

(39)

This result is clearly different from Eq. 33 because now, the linear behavior with $|\gamma_T| T_h$ is also present. Next, we evaluate this quadratic equation in $\sigma$ for various magnitudes of the thermal gradients and show that it is identical to the LSA results for large thermal gradients. By defining $f = \gamma_T^2 + A/2\pi h_0^2$ and $g = (3|\gamma_T| T_h)/h_0$, the roots of the dispersion relation are:

$$\sigma_{\pm} = -\frac{h_0^3 k^2}{6\eta} (f + g) \pm \frac{h_0^3 k^2}{6\eta} \sqrt{(f + g)^2 - g^2}$$

(40)

1. Minimum dissipation approach for classical case (i.e. $T_h = 0$)

By substituting $T_h = g = 0$ in Eq. 40, the resulting relevant root is:

$$\sigma_- = -\frac{h_0^3 k^2}{3\eta} (\gamma_T^2 + \frac{A}{2\pi h_0^2})$$

(41)

As expected, this result is identical to the result for the classical dewetting instability.

2. Minimum dissipation approach for strong thermal gradients

In the case when the magnitudes of the thermal gradients are larger than the attractive dispersion forces, i.e. for example when $3|\gamma_T| T_h \geq A/2\pi h_0^2$, then we have $|g| > |f|$. This is the condition found in the experimental cases reported earlier [29, 30], and we can obtain an approximate solution from Eq. 40 as follows:

$$\sigma_{\pm} \approx -\frac{h_0^3 k^2}{6\eta} (f + g) \pm \frac{h_0^3 k^2}{6\eta} \sqrt{g^2 - g^2} = -\frac{h_0^3 k^2}{6\eta} (f + g)$$

(42)

or

$$\sigma_{TC}^{TH} = -\frac{h_0^3 k^2}{3\eta} (\gamma_T^2 + \frac{A}{2\pi h_0^2})$$

(43)

From Eq. 43, the characteristic wavelength $\Lambda_{TC}^{TH}$ obtained from the maxima in the dispersion given by $d\sigma/dk = 0$ is:

$$\Lambda_{TC}^{TH} = \sqrt{\frac{16\pi^2 \gamma}{A + 6\pi |\gamma_T| T_h h_0^2}}$$

(44)

Comparing with the LSA result, Eq. 27, the only difference is in the factor of two multiplying the thermal gradient term. More importantly, the functional dependence on $h_0$, $\alpha$, $\gamma$, and $|\gamma_T| T_h$ remains the same, confirming that the minimum dissipation approach gives similar physical characteristics for the dewetting instability. An important benefit of utilizing the thermodynamic approach is also evident here. From the above dissipation analysis it is clear that there are multiple choices for the dewetting pathway in regards to the rate of dissipation. However, the instability clearly picks the path which minimizes the rate of this dissipation, or in other words, minimizes the overall rate at which energy is lost in the dewetting process. We have also plotted the behavior of the dispersion relation, Eq. 43 for Co films on SiO$_2$ substrates with the various materials parameter values being: Hamaker coefficient $A = -1.41 \times 10^{-18}$ J, $\gamma = 1.88$ J/m$^2$ and $|\gamma_T| = -4.8 \times 10^{-3}$ J/m$^2$ – K. Fig. 1a plots the growth rate $\sigma$ versus wave number $k$ for the dispersion relation Eq. 43. The data was evaluated for Co film of thickness 8 nm and various values of the gradient $T_h$, including $T_h = 0$, $T_h > 0$ and $T_h < 0$, as indicated on the plot. In Fig. 1b) we have plotted the characteristic length scale $\Lambda_{TC}^{TH}$ for Co films on SiO$_2$ as a function of varying thickness and various $T_h$. The decrease in length scale with increase in the magnitude of $T_h < 0$ is evident. In Fig. 1c) the cut-off wavelength $\Lambda_{cut-off}$ as a function of varying thickness and various $T_h$ is plotted. The cut-off wavelength corresponds to the intersection of the growth rate with the wave number axis in Fig. 1a).
3. Minimum dissipation approach for weak thermal gradients

In the case when the magnitudes of the thermal gradients are smaller then the attractive dispersion forces, i.e. for example when $3 | \gamma T_b | < | A/2 \pi \eta k^2 |$, then we have $| g | < | f |$. In this situation, we can approximate Eq. 40 as follows:

$$\sigma_e \approx \frac{h_0^2 k^2}{6 \eta} (f + g) \pm \frac{h_0^2 k^2}{6 \eta} \sqrt{f^2 - g^2} \approx \frac{h_0^2 k^2}{6 \eta} (f + g) \pm \frac{h_0^2 k^2}{6 \eta} f \left(1 - \frac{g^2}{2f^2}\right)$$

(45)

where we have used the binomial approximation $(1 - (g/f)^2)^{1/2} \sim (1 - g^2/2f^2)$. Here we find again that the dispersion is considerably different from the LSA result of Eq. 26.

IV. CONCLUSION

We have theoretically evaluated the classical and thermocapillary dewetting instability in thin fluid films via a thermodynamic approach. In this case, the rate of change of free energy is equated to the viscous dissipation in the thin film. The thermodynamic approach leads to an analytical expression for the dispersion without the need for explicit solution of the height evolution dynamical equation from NS within the lubrication approximation. We have compared results from this approach to existing results obtained by linearization of the fluid dynamics of the thin film. For the case of classical dewetting in the presence of surface tension and long range attractive forces, the thermodynamic approach predicts identical behavior to that from linear analysis. We have also evaluated dewetting in the presence of film-thickness dependent temperature variations. Such a situation can be found during dewetting of thin metallic films melted by a nanosecond ultraviolet pulsed laser. In this condition, a film thickness dependent reflection and absorption leads to thermocapillary forces along the plane of the film. In this scenario we found that the thermodynamic approach agrees with linear analysis provided the minimum viscous dissipation is evaluated. The fluid flow condition that gives minimum viscous dissipation is one where the film-substrate tangential stress is zero. In the context of tension and long range attractive forces, the thermodynamic approach predicts identical behavior to that from linear analysis. This results shows that the thermodynamic approach based on evaluating the rates of free energy change and energy loss is a simple but potentially powerful way to gain physically meaningful insight into such spontaneous pattern formation processes.

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Figure captions

- **Figure 1**: (a) Plot of the growth rate versus wave number for the dispersion relation obtained from the dissipation approach for strong thermal gradients. The data was evaluated for Co film of thickness 8 nm and various values of the gradient $T_h$, as indicated on the plot. (b) Plot of the characteristic length scale $\Lambda_{TH}^c$ for Co films on SiO$_2$ as a function of various $T_h$. (c) Plot of the cut-off wavelength $\Lambda_{cut-off}$ for Co films on SiO$_2$ as a function of various $T_h$. The cut-off wave number corresponds to the intersection of the rate with the wave number axis in Fig. (a).
