THE NANOSCALE INSTABILITY DRIVING LEIDENFROST FILM COLLAPSE

TOM Y. ZHAO† AND NEELESH A. PATANKAR†,*

ABSTRACT. Above a critical temperature known as the Leidenfrost point (LFP), a heated surface can suspend a liquid droplet above a film of its own vapor. The insulating vapor film can be highly detrimental in metallurgical quenching and thermal control of electronic devices, but may also be harnessed to reduce drag and generate power. Manipulation of the LFP has occurred mostly through experiment, giving rise to a variety of semi-empirical models that account for the Rayleigh-Taylor instability, nucleation rates, and superheat limits. However, a truly comprehensive model has been difficult given that the LFP varies dramatically for different fluids and is affected by system pressure, surface roughness and liquid wettability. Here, we identify the vapor film instability for small length scales that ultimately sets the collapse condition at the Leidenfrost point. From a linear stability analysis, it is shown that the main film stabilizing mechanisms are the liquid-vapor surface tension, viscous transport of vapor mass, and evaporation at the liquid-vapor interface. Meanwhile, van der Waals interaction between the bulk liquid and the solid substrate across the vapor phase drives film collapse. This physical insight into vapor film dynamics allows us to derive an ab-initio, mathematical expression for the Leidenfrost point of a fluid. The expression captures the experimental data on the LFP for different fluids under various surface wettabilities and ambient pressures. For fluids that wet the surface (small intrinsic contact angle), the expression can be simplified to a single, dimensionless number that encapsulates the nanoscale instability governing the LFP.

1. Introduction

As a surface is superheated above the boiling point of an adjacent fluid, vapor bubbles nucleate and grow. The boiling behavior of the liquid phase undergoes a fundamental change at a critical temperature known as the Leidenfrost point. Beyond this point, a film of insulating vapor forms between the liquid and the surface that suppresses heat transfer from the solid material. This heat flux reduction can be highly detrimental in the quenching of metal alloys by extending cooling rates and precluding the desired increase in strength and hardness. Alternatively, film boiling may be used to promote drag reduction as well as enable power generation through self-propulsion. Thus, modulation of the LFP through fluid choice, surface texture and chemistry for the specific application is crucial.

(†) Northwestern University, Department of Mechanical Engineering: 2145 Sheridan Road, Evanston, Illinois 60208, USA
(*) E-mail: n-patankar@northwestern.edu
On a fundamental level, the physical mechanism responsible for the LFP is still uncertain. Many theoretical frameworks have been used to characterize the Leidenfrost effect and estimate the LFP, including hydrodynamic instability, superheat spinodal limits, and the change of liquid wettability on the heated surface with temperature. A thermocapillary model has also been proposed that attributes the film instability to fluctuations at micron length scales; however, the analysis posits that the thermocapillary effect is the dominant destabilizing term, which does not explain the significant change in LFP on surfaces with different wettabilities. For example, the LFP of water can vary from 300°C for hydrophilic surfaces to 145°C on hydrophobic surfaces.

In this work, we introduce a stability analysis of the vapor film at the nanoscale regime. The dominant destabilizing term arises from the van der Waals interaction between the bulk liquid and the substrate across a thin vapor layer. On the other hand, liquid-vapor surface tension, viscous transport of vapor, and evaporation at the two phase interface stabilize the film. The competition between these mechanisms gives rise to a comprehensive description of the LFP as a function of both fluid and solid properties. For fluids that wet the surface, such that the intrinsic contact angle is small, a single nondimensional number can be derived that encapsulates the nanoscale instability determining the Leidenfrost point.

Note that the literature has proposed different names for the critical temperature associated with a droplet levitating on a heated plate (Leidenfrost point) versus the critical temperature for vapor film formation in pool boiling (minimum film temperature). The Leidenfrost point has been shown to be equivalent to the minimum film boiling temperature for saturated liquids on isothermal surfaces. In this work, the term LFP will be used for both cases as a matter of convenience, with the understanding that no undercooling is applied to the liquid phase for pool boiling scenarios unless explicitly stated.

2. Film Instability

There are many approaches to examine the stability of a vapor film adjacent to a superheated wall in two dimensions. Models have been developed with a base solution imposing static equilibrium, where the interface is at the saturation temperature corresponding to the imposed, far field liquid pressure. Here, we consider the thickness of the vapor film to be in dynamic equilibrium, as in a vertical plate configuration or vapor under a droplet. This appears to be a more general analysis since under experimental settings, droplet levitation occurs over a film that is continuously replenished by evaporation and depleted through escape of the buoyant vapor phase. Similarly in a horizontal setup for pool boiling, bubbles pinch off the film, necessitating a nonzero rate of evaporation to sustain a constant mean film thickness.

Fig. 1 shows the problem of film boiling on a vertical plate as studied by Burmeister and Carey. The vapor forms a laminar layer at the wall, with evaporation at the liquid interface sustaining the buoyant transport of vapor mass away from the base of the plate. The surrounding liquid is saturated and motionless with its properties fixed at the saturation temperature. The properties of vapor are assumed to be constant at the superheated wall temperature.
2.1. Governing Equations. The mass, momentum and energy conservation equations in the vapor domain are:

\begin{equation}
\frac{\partial \bar{u}_V}{\partial x} + \frac{\partial \bar{v}_V}{\partial y} = 0
\end{equation}

\begin{equation}
\bar{u}_V \frac{\partial \bar{u}_V}{\partial x} + \bar{v}_V \frac{\partial \bar{u}_V}{\partial y} = -\frac{1}{\rho_V} \frac{\partial \bar{\Phi}}{\partial x} + \frac{\Delta \rho g}{\rho_V} + \frac{\mu_V}{\rho_V} \frac{\partial^2 \bar{u}_V}{\partial y^2}
\end{equation}

\begin{equation}
\bar{u}_V \frac{\partial \bar{\Theta}_V}{\partial x} + \bar{v}_V \frac{\partial \bar{\Theta}_V}{\partial y} = \frac{k_V}{\rho_V c_{p,V}} \frac{\partial^2 \bar{\Theta}_V}{\partial y^2}
\end{equation}

where the parameters \( \mu, \rho, k, g \) and \( c_p \) represent the dynamic viscosity, density, thermal conductivity, gravitational acceleration and specific heat of the fluid, respectively. The term \( \Delta \rho = \rho_L - \rho_V \), the subscripts \( L \) and \( V \) denote the liquid and vapor field, and the temperature has been normalized as \( \bar{\Theta} = \frac{T - T_s}{T_w - T_s} \), the difference between the temperature field and the saturation temperature \( T_s \) at the interface over the difference between the wall temperature \( T_w \) and \( T_s \).

The generalized pressure term \( \bar{\Phi} \) takes into account both the pressure arising from surface tension forces as well as van der Waals interactions. To first order in the base solution, these terms are negligible since the liquid-vapor interface is assumed to be locally parallel to the wall\[19,20\], this implies \( \bar{\Phi} \approx 0 + \Phi' \), where the primed variable denotes a perturbed component. Additionally, the temperature equation is modeled as steady in the basic solution and only exhibits a time varying term in the perturbation equation. The boundary conditions at the superheated wall and the liquid-vapor interface at \( \bar{\delta}(x) \) are given by:

\begin{equation}
\text{at } y = 0, \quad \bar{u}_V = \bar{v}_V = 0, \quad \bar{\Theta}_V = 1
\end{equation}
at $y = \delta$, \[ \bar{u}_V = \bar{u}_L = 0, \quad \bar{\Theta}_V = 0 \]

\[ \rho \bar{u}_V \frac{d \delta}{dx} - \rho \bar{v}_V = \rho \bar{u}_L \frac{d \delta}{dx} - \rho \bar{v}_L \]

\[ \bar{u}_V + \bar{v}_V \frac{d \delta}{dx} = \bar{u}_L + \bar{v}_L \frac{d \delta}{dx} \]

Eqn. 6 enforces mass conservation in the direction normal to the interface, whereas eqn. 7 ensures that tangential component of velocity is continuous. The energy and mass balance equation at the interface is:

\[ \rho \bar{V} \frac{\partial \bar{\delta}}{\partial t} + \frac{\partial}{\partial x} \int_0^\delta (\rho \bar{u}_V \bar{v}_V dy) = - \frac{k_{LV}}{h_{LV}} \frac{\partial \bar{\Theta}_V}{\partial y} \bigg|_{y=\delta} \]

where $h_{LV}$ is the latent heat of vaporization. In the base state, the time variation of the film thickness is taken to be negligible, \[ \frac{d \bar{\delta}}{dt} \approx 0 + \bar{u}_V' \]

2.2. Basic Flow. The basic flow field can be found approximately by using an integral expansion method, which is described in full detail by Burmeister. After introducing the normalized variable $\eta = y/\delta$, we can determine the velocity ($u_V$) and temperature field ($\Theta_V$) in the base solution:

\[ u_V = \frac{\Delta \rho \rho_{LV}^2}{2 \mu_V} (\eta - \eta^2) \]

\[ \Theta_V = \frac{T_V - T_s}{T_w - T_s} = 1 + (-1 - \frac{1 - c}{2} \eta + \frac{1 - c}{2} \eta^2 \]

where $c$ can be found by solving the quadratic expression:

\[ \frac{1}{3} c_{p,V} \Delta T = 1 - \frac{3}{10} (1 - c) \]

and $\Delta T = T_w - T_s$. For typical Jakob numbers around $Ja = \frac{c_{p,V} \Delta T}{h_{LV}} = \frac{1}{10}$, $c$ can be found from a simplified linear equation $c = 1 - \frac{1}{3} \frac{c_{p,V} \Delta T}{h_{LV}}$. Using this approximation, the film thickness $\delta$ is described by:

\[ \delta = 2 \left(1 - \frac{1}{3} c_{p,V} \Delta T \right)^{\frac{1}{4}} \left( \frac{x \Delta T \mu_{LV} k_V}{\rho_{LV} h_{LV} g \Delta \rho} \right)^{\frac{1}{4}} \]

Note that to first order, the velocity and temperature fields as well as the film thickness are steady.

2.3. Linearized Equations. The base solutions for the velocity, temperature and film thickness are perturbed, giving rise to the following linearized equations:

\[ \frac{\partial u'}{\partial x} + \frac{\partial v'}{\partial y} = 0 \]

\[ u' \frac{\partial u'}{\partial x} + u' \frac{\partial u'}{\partial x} + v' \frac{\partial u'}{\partial y} + v' \frac{\partial u'}{\partial y} = - \frac{1}{\rho_V} \frac{\partial \bar{\Psi}'}{\partial x} + \frac{\mu_V}{\rho_V} \frac{\partial^2 u'}{\partial y^2} \]

\[ \frac{\partial \bar{\Theta}'}{\partial t} + u' \frac{\partial \bar{\Theta}'}{\partial x} + u' \frac{\partial \bar{\Theta}'}{\partial x} + v' \frac{\partial \bar{\Theta}'}{\partial y} + v' \frac{\partial \bar{\Theta}'}{\partial y} = \frac{k_V}{\rho_V c_{p,V}} \frac{\partial^2 \bar{\Theta}'}{\partial y^2} \]

The boundary conditions at the wall are:

at $y = 0$ \[ u_V' = v_V' = 0, \quad \bar{\Theta}_V' = 0 \]
At the perturbed interface location $\delta'$, the tangential velocity condition (eqn. 7) after applying the locally parallel approximation $\frac{d\delta'}{dx} \approx 0$ gives:

$$u'_V + \frac{\delta'}{\delta} \frac{\partial u}{\partial \eta}|_{\eta=1} = \text{liquid side}$$

Analogous to the base solution, the perturbed velocity is expanded in powers of $\eta$.

$$u'_V = a'_0 + a'_1 \eta + a'_2 \eta^2$$

at $\eta = 0 \quad u'_V = 0 \rightarrow a'_0 = 0$

The terms $a'_1$ and $a'_2$ can be found as functions of the fluid properties and the generalized pressure gradient $\frac{\partial \Phi'}{\partial x} = \frac{\partial \Phi'}{\partial x} + \frac{\partial \phi'}{\partial x}$.

$$a'_1 = \left( \frac{\Delta \rho g \delta' \delta'^2}{2 \mu_V} - \frac{\partial \Phi'}{\partial x} \delta'^2 \right)$$

$$a'_2 = \frac{\partial \Phi'}{\partial x} \delta'^2$$

The pressure gradient arises from the liquid-vapor surface tension $\sigma_{LV}$ at the two phase interface due to capillary pressure induced by local nonzero curvature:

$$\frac{\partial \delta'}{\partial x} = -\sigma_{LV} \frac{d^3 \delta'}{dx^3}$$

This implies that positive curvature corresponds to the center of curvature lying in the vapor domain, such that the vapor bulges into the liquid. Here, we also introduce the disjoining pressure term $\phi$, which describes the van der Waals interaction between the fluid and the substrate:

$$\phi = \frac{A}{6\pi \delta^3}$$

The streamwise derivative of this term is negligible in the base state under the locally parallel interface approximation. The Hamaker constant $A$ is typically positive, denoting attractive interactions between dipoles\[21\]. The perturbed component is:

$$\frac{\partial \phi'}{\partial x} = -\frac{A}{2\pi \delta^4} \frac{d \delta'}{dx}$$

This gives an expression for the perturbed, generalized pressure term evaluated at the liquid-vapor interface.

$$\frac{\partial \Phi'}{\partial x} = \frac{\partial \phi'}{\partial x} + \frac{\partial \phi'}{\partial x} = -\sigma_{LV} \frac{d^3 \delta'}{dx^3} - \frac{A}{2\pi \delta^4} \frac{d \delta'}{dx}$$

Next, the expanded perturbed temperature is:

$$\Theta'_V = b'_0 + b'_1 \eta + b'_2 \eta^2 + b'_3 \eta^3$$

From the boundary condition (eqn. 4) and energy conservation equation (eqn. 11) at $\eta = 0$, we find that $b'_0 = b'_2 = 0$. Similarly, the temperature conditions (eqn. 5
This leads to the general expression for the temporal growth rate \( \lambda \) at \( y = \delta \):

\[
\frac{\delta \partial \delta'}{4 \partial t} + \frac{1}{4} (1-2b_3) \frac{\partial \delta'}{\partial t} + \left( \frac{1}{6} - \frac{2b_3}{15} \right) \frac{\Delta \rho g \delta'^2}{\mu V} \frac{d \delta'}{d x} + \left( \frac{1}{12} - \frac{b_3}{20} \right) \left( \frac{\delta^3}{2 \mu V} + \frac{A}{2 \pi \delta^2} \frac{d^2 \delta'}{d x^2} \right)
\]

\[
\frac{a_1}{30} (1-2b_3) \frac{d \delta'}{d x} + \frac{a_1 \delta}{20} \frac{d b_1'}{d x} = \frac{3k_v}{\rho c_p,\nu \delta^2} \delta' - \frac{3k_v}{\rho c_p,\nu \delta} \delta' b_1' = 0
\]

The time evolution equation for the perturbed \( \delta' \) follows from eqn. 8 and the expressions for \( u'_V \) and \( \Theta'_V \) (eqn. 12 and 14):

\[
\rho V \frac{\partial \delta'}{\partial t} + \rho V \Delta \rho g \delta'^2 \frac{d \delta'}{d x} + \rho V \delta^3 \Delta \rho \gamma \frac{d \delta'}{d x} + \frac{\rho V A}{d t} \frac{d^2 \delta'}{d x^2} - 3k_v \Delta T \frac{d \delta'}{d x} = \frac{2k_v}{h_{LV} \delta} \delta' b_1' = 0
\]

The perturbation equations [15 and 16] give two homogeneous conditions for \( \delta' \) and \( b_1' \). The perturbations can now be expressed in terms of normal modes:

\[
\delta' = \delta'_0 \exp(i(kt + \omega t))
\]

\[
b_1' = b_1'_0 \exp(i(kt + \omega t))
\]

To avoid introducing new notation, we will represent the amplitudes without subscripts \( \delta'_0 \rightarrow \delta' \) and \( b_1'_0 \rightarrow b_1' \). Here, \( k \) is the wave number and \( \omega \) is the time rate of growth of the perturbation. We combine eqn. [15 and 16] to obtain a single equation with the coefficient \( \delta' \). To simplify the representation, we introduce the following nondimensional parameters:

\[
\pi_{LP} = \frac{3A^2 h_{LV} \rho V}{(24\pi)^2 \delta^3 k_v \mu V \Delta T \sigma_{LV}}
\]

\[
\pi_{LB\sigma_{LV}} = \sqrt{\frac{A}{\pi \sigma_{LV}}} \left( \frac{\Delta \rho g \delta^2 h_{LV} \rho V}{2k_v \mu V \Delta T} \right)
\]

\[
k'' = k \delta^2 \sqrt{\frac{4\pi \sigma_{LV}}{A}}
\]

\[
\omega' = \omega \left( \frac{h_{LV} \rho V \delta^2}{k_v \Delta T} \right)
\]

This leads to the general expression for the temporal growth rate \( i\omega \) of the perturbation after eliminating \( b_1' \) from eqn. [15 and 16]

\[
\left( \frac{i\omega'}{8} + \frac{3}{2Ja} \right) \left( i\omega' + \frac{k'' \pi_{LB\sigma_{LV}}}{4} + \frac{3}{2Ja} \pi_{LP} - 2\pi_{LP} k'' + 3 \right)
\]

\[
+ \frac{i\omega'}{4} + \frac{k''}{20} \left( 1+c \right) \pi_{LB\sigma_{LV}} + \frac{k''}{20} \left( 7 + c \right) \pi_{LP} + \frac{3}{10} - \frac{3}{Ja} = 0
\]

The marginal state occurs when the real part \( \text{Re}(i\omega) = 0 \), separating zones of stability (\( \text{Re}(i\omega) < 0 \)), where the perturbation amplitude decays in time, from regions of instability (\( \text{Re}(i\omega) > 0 \)), where the base state becomes unstable (Fig. 2a). Note that only three dimensionless numbers \( J a, \pi_{LP} \) and \( \pi_{LB\sigma_{LV}} \) govern the stability of the perturbed solution. Due to the inclusion of van der Waals interactions, the buoyancy terms described by \( \pi_{LB\sigma_{LV}} \) become negligible at nanoscale, as will be discussed in the next section.

This analysis incorporated time variation and convective transport in the energy equation. We can obtain a simpler expression for the stability problem by only
considering the temporal evolution of the film thickness and assuming quasi-steady conduction for the temperature field:

\[
    i\omega' = -(k''^{4}\pi_{LP} - 2k''^{2}\pi_{LP} + 1) - ik''\pi_{LB}\sigma_{LV}\frac{4}{\pi_{LP}}
\]

The diffusive expression (eqn. 18) is a good estimate to the full stability equation (eqn. 17) for small Jakob numbers, as demonstrated in Fig. 2. Since the non-dimensional parameters are calculated from the vapor properties at the superheated wall temperature, the Jakob number is small \((Ja \lesssim \frac{1}{10})\) for the vapor phase of most fluids, implying that the thermal energy imparted by the heated solid is predominantly consumed through the latent heat of phase change rather than as sensible heat in raising the temperature of the vapor.

The Leidenfrost point corresponds to the lowest, critical \(\pi_{LP, crit}\) below which the flow becomes unconditionally stable for all values of \(k''\). For eqn. 17 a good approximation for the critical \(\pi_{LP}\) can be derived by noting that due to how we scaled the dimensionless parameters, \(\pi_{LP, crit}\) occurs at \(k'' = 1\). This leads to an algebraic equation for \(\pi_{LP, crit}\):

\[
    \left(\frac{Ja}{10}(\frac{7}{3} + c) + 1\right)\pi_{LP, crit} - 1)(1 + \frac{Ja}{4} + \frac{Ja}{6}c - \frac{Ja}{12}\pi_{LP, crit})^2
    = \left(\frac{3\pi_{LB}\sigma_{LV}}{20}\right)^2 \left(\frac{Ja}{12}\right)^2 (1 + \frac{Ja}{9}(2 + c)) \left(\frac{1}{3} + \frac{2c}{3} - \pi_{LP, crit}\right)
\]

Eqn. 19 was verified against a numerical solution to the full stability equation (eqn. 17) with \(\text{Re}(\omega) = 0\), and was found to give the same solution for \(\pi_{LP, crit}\) up to machine precision for all parameter sets tested (Fig. 2b). For small Jakob numbers, Fig. 2c shows that the critical \(\pi_{LP}\) can also be estimated from the diffusive expression (eqn. 18).

\[
    \pi_{LP, crit} = 1
\]

2.4. Stabilizing Terms. The diffusive approximation to the critical \(\pi_{LP}\) (eqn. 20) reveals that the main stabilizing terms are the liquid-vapor surface tension \(\sigma_{LV}\), the evaporative phase change that replenishes local vapor mass \(k_{LV}\Delta T\rho_{LV}\), and the viscous shear \(\mu\) that reduces mass transport away from any given point in the vapor field.

The liquid-vapor surface tension acts as a restoring force against oscillatory modes imposed on the basic, locally-parallel solution. Positive curvature of the liquid-vapor interface with its center in the vapor region (curving into the liquid), induces high pressure locally with an adjacent low pressure zone due to the negative curvature of the continuous two phase interface. This creates a pressure gradient that attempts to restore the basic state by dampening all possible oscillatory frequencies.

Similarly, a perturbed interface that bulges into the vapor steepens the thermal gradient in the vapor film, triggering an increase in the rate of evaporation locally that restores the base state and vice versa. Viscous shear is larger for smaller film thicknesses, therefore reducing mass transport away from a local bulge into the vapor domain and enhancing transport away from a bulge into the liquid field; this also acts to dampen perturbed modes.
Figure 2. The stability of the perturbed solution.

a. The variation of \( \text{Re}(i\omega) \) with \( \pi_{LP} \) and the dimensionless wavenumber \( k'' \). A critical \( \pi_{LP} \) can be defined, for which lower values lead to unconditional stability, and greater values allow the coexistence of stable and unstable zones. b. The Jakob number vs the critical \( \pi_{LP} \), as predicted by the numerical solution to the full stability solution (eqn. 17) and by assuming the centerline for \( k'' \) is at 1 (eqn: 19). The agreement is excellent. c. The marginal stability curves are calculated by taking the locus of points where the real value of \( i\omega \) changes sign. The diffusive expression (eqn. 18) is a good approximation for small Jakob numbers.

2.5. van der Waals Interaction. The heterogeneous Hamaker constant \( A_{SVL} \) is used to characterize the van der Waals dispersion forces between an uncharged surface and an adjacent liquid separated by vacuum. It is incorporated into this analysis via the generalized pressure gradient (eqn: 13). From the diffusive expression of the perturbation stability (eqn. 18), it is shown that these dispersion forces between the liquid and solid substrate across the vapor film is the only destabilizing term for attractive interactions \( A > 0 \). The film is unconditionally stable if the interaction is purely repulsive \( A < 0 \). The former case holds in general for a liquid separated from a solid by a vacuum or an intermediate gas phase.\(^{22,23}\)

The relationship between the heterogeneous Hamaker constant and the contact angle \( \theta \) of the substrate has been derived using Lifshitz theory\(^{24,25}\):

\[
1 + \cos(\theta) = \frac{A_{SVL}}{12\pi\sigma_{LV}H_{SVL}}
\]

where \( H_{SVL} \) is the equilibrium contact separation between the liquid and the solid substrate and takes on values in the order of magnitude of 1 nm for most materials. Eqn. 21 can thus be used to account for the effect of surface wettability on the stability of the perturbed solution. As the van der Waals interaction only plays a significant role for film thicknesses that have reached the same order of magnitude as \( H_{SVL} \), we approximate the ratio \( \frac{H_{SVL}}{\delta} \approx 1 \).

In this nanoscale regime, the neutral curve described by the full perturbation solution (eqn: 17) is insensitive to \( \pi_{LB\sigma_{LV}} \), which encapsulates the buoyancy force on the vapor film and is on the order of \( 1e-14 \). The diffusive expression of the perturbation equation (eqn. 18) has an explicit dependence on \( \pi_{LB\sigma_{LV}} \) only in the imaginary part of the temporal growth rate, such that the marginal state predicted is completely agnostic to changes in \( \pi_{LB\sigma_{LV}} \). This implies that the stability criterion (eqn. 19 or 20) can be applied to capture the Leidenfrost point on plates of arbitrary
orientation, as the direction and magnitude of the gravitation field does not play a significant role in the instability mechanism examined.

3. Experimental verification

To compare against experimental data, eqn. 20 for the critical $\pi_{LP}$ can be rewritten in terms of material properties:

$$\frac{3}{(24\pi)^2} \left( \frac{1}{\delta} \right)^4 \frac{h_{LV} \rho_V \delta}{\sigma_{LV}} A^2 \frac{1}{k_V \Delta T \mu_V} = 1$$

Substituting in eqn. 21, we obtain the corresponding expression for the LFP in terms of the intrinsic contact angle on the substrate.

$$\frac{3}{4} \left( \frac{H_{SVL}}{\delta} \right)^4 \left( \frac{h_{LV} \rho_V \delta}{\sigma_{LV}} \right) (1 + \cos(\theta))^2 \frac{\sigma_{LV}^2}{k_V \Delta T \mu_V} = 1$$

where we have defined two new nondimensional parameters that we will show to be significant:

$$\pi_1 = \frac{\sigma_{LV}^2}{k_V \mu_V \Delta T}$$
$$\pi_2 = \frac{h_{LV} \rho_V \delta}{\sigma_{LV}}$$

Eqn. 23 provides an explicit relationship between the intrinsic contact angle of a fluid on a substrate and the Leidenfrost point for the system. Since each fluid property ($k_V(T), \mu_V(T), \sigma_{LV}(T)$, etc.) is calculated at the superheated wall temperature, the left hand side of eqn. 23 is in general a nonlinear function of temperature. The temperature at which eqn. 23 is satisfied corresponds to the predicted LFP; this can be found numerically with the temperature and pressure dependent fluid properties available from databases like NIST and tabulations from literature.

3.1. Surface dependence of the LFP. The LFP for water has been demonstrated to vary dramatically with changes in the liquid wettability of the solid surface. Fig. 3 shows that the diffusive prediction of the LFP (eqn. 23) accurately captures the relationship between the LFP and the contact angle as delineated by experiments. Physically, larger contact angles indicate a hydrophobic substrate, which exhibits less attractive van der Waals interaction with the bulk liquid and presents a smaller destabilizing effect to the vapor film; the LFP thus decreases to near the boiling point. Without considering van der Waals interaction between the liquid and substrate surfaces, such a relationship cannot be explained or predicted from first principles.

Further evidence of the significant role played by van der Waals forces in governing the LFP arises from X-ray imaging of the vapor film collapse. Images spanning the film lifespan between formation and collapse showed that film collapse on the macroscopic level is preceded by submicron length scale vapor film thicknesses where the bulk liquid appears to wet the substrate. Although instabilities on the micron scale and above perturb the liquid-vapor interface and induce frequent local contact between the liquid and solid, only when the vapor film becomes unstable...
3.2. **Fluid dependence of the LFP.** For most experimentally available data on the Leidenfrost point, the contact angle of the fluid on the substrate material is low, around $\theta \approx 20^\circ$. Nonetheless, the Hamaker constant must be found to determine the equilibrium separation $H_{SVL}$. Although the assumption $H_{SVL} \approx 1$ is made, the base film thickness $\delta$ still needs to be incorporated into our instability expression via $\pi_2$ (eqn: 25). We can find the homogeneous Hamaker constant of the fluid (acetone, ethanol, benzene, etc.) and the substrate (gold, aluminum, copper), and take the geometric mean to obtain the heterogeneous value $^{23,34}$. From the relationship between the surface energy and homogeneous Hamaker constant, we can obtain the homogeneous contact separations via:

$$\sigma_{LV} = \frac{A_{LV,L}}{24\pi H_{LV,L}^2}$$
Figure 4. The equilibrium contact surface separation for the fluid (alkanes), surface (gold) and the heterogeneous value corresponding to the Leidenfrost point. Note that the equilibrium separation $H_{LVL}$ is reported at the respective Leidenfrost temperatures of each alkane species, whereas Drummond et. al. listed $H_{LVL}$ at the same temperature. The temperature dependence of $H_{SVS}$ is assumed to be small over the range of temperatures corresponding to the LFP of the alkane series, which is much lower than the melting point of gold.

The heterogeneous contact separation have been estimated as the arithmetic or geometric mean of the homogeneous values, although these means may not provide a good approximation for the actual $H_{SVL}$ in general. Nonetheless, for our theory to be physically consistent, the heterogeneous contact separation corresponding to the experimental Leidenfrost temperatures must be between the two bounding homogeneous values. Figure 4 shows that for the alkane family, this condition $H_{SVS} < \delta \approx H_{PVL} < H_{LVL}$ is satisfied, and the arithmetic and geometric means provide a reasonable estimate to the actual heterogeneous value.

Drummond has shown that as the chain length of the alkane species increases, the contact angle increases correspondingly. This suggests that longer chain alkanes in the liquid phase have unfavorable energetic interactions with a given substrate (greater liquid-solid surface energy $\sigma_{SL}$) compared to small chain alkanes on the same solid material. The heterogeneous, equilibrium distance $H_{PVL}$ therefore tends to increase with the straight chain length of the alkane species, moving from near the solid separation $H_{SVS}$ toward the liquid value $H_{LVL}$.

Figure 4 shows that it is possible to determine either the heterogeneous Hamaker constant given the Leidenfrost point for a fluid on a solid substrate, or vice versa.

$$\sigma_{SV} = \frac{A_{SVS}}{24\pi H_{SVS}^2}$$
with knowledge of the homogeneous Hamaker constants of both species. In general, experimental data on the homogeneous Hamaker constants may not be available for a fluid or substrate of interest. Here, we note an avenue for simplification: it is observed that the nondimensional quantity $\pi_2 = \frac{h_{LV}\rho V}{\sigma_{LV}}$ in the diffusive expression is around 0.06 for most fluids at their respective Leidenfrost temperatures. This suggests that there exists a functional dependence $H_{SVL} = F\left(\frac{h_{LV}\rho V}{\sigma_{LV}}\right)$. Additionally, most experimental setups in the film boiling regime feature fluids that wet the surface in contact, such that their intrinsic contact angle are small ($\theta \approx 20^\circ$)\cite{28}. From the diffusive expression (eqn. 23), the above approximations leads to a simplified, dimensionless prediction to the Leidenfrost point for fluids/substrate systems with low, intrinsic contact angles:

\begin{equation}
\pi_1 = \frac{\sigma_{LV}^2}{k_{LV}\Delta T_{LV}} \approx 6
\end{equation}

Fig. 5 shows that the temperature at which this equality is satisfied captures the experimental data on the LFP for a variety of different fluids, including cryogens and liquid metals. The single dimensionless number describes the terms that stabilize the vapor film, including surface tension, phase change and viscous transport, while the critical value corresponding to the LFP denotes the destabilizing effect of
attractive van der Waals interaction between the bulk liquid and solid substrate. Larger values of $\pi_1$ above the critical imply the system is in the film boiling regime, since the stabilizing terms dominate.

3.3. Pressure dependence of the LFP. Experimental work has shown that the LFP depends on the ambient pressure applied, such that the Leidenfrost temperature gradually increases from near the boiling point towards the critical point of the fluid. For low contact angle fluid/substrate systems, we find that $\pi_2(1 + \cos(\theta))^2$ scales linearly with pressure such that the LFP corresponds to:

$$\pi_1 \approx 6 \frac{p_{\text{ref}}}{p_{\text{applied}}}$$

where $p_{\text{ref}}$ and $p_{\text{applied}}$ are 1 atm and the applied, operating pressure, respectively. Figure 6 demonstrates that eqn. 27 captures the LFP for both subatmospheric and superatmospheric pressures up to the critical point.

4. Conclusion

The dynamic stability of a vapor film on a heated vertical wall under the effects of gravity were considered. The only possible instability at nanoscale was driven by attractive van der Waals interaction between the bulk liquid and the substrate, which could be stabilized by the liquid-vapor surface tension, evaporative phase change and viscous transport. The marginal or neutral state can be found analytically (eqn. 19) for the most general case, or simplified for small Jakob number flows to a diffusive approximation (eqn. 20). The resulting theoretical solution for
the LFP captures the variation of experimental data with surface wettability, fluid properties and pressure.

A single, dimensionless number $\pi_1$ is found to encapsulate the physical instability mechanism of the Leidenfrost phenomenon for wetting fluids. The value of $\pi_1$ with respect to the critical denotes regimes in which the vapor film is stable or unstable, providing a useful characterization of both the thermodynamic state and the physical means by which transition to the pool boiling regime occurs.

This insight into the nanoscale mechanisms inducing the transition from film to nucleate boiling enables control of the phase adjacent to the surface\cite{51}. It would be of interest to extend the instability mechanism towards surface roughness, which experiment has shown to effect dramatic changes in the LFP beyond what can be explained by variation in surface wettability\cite{5;14;47}. In addition, a theoretical treatment of the Nukiyama temperature corresponding to the critical heat flux may reveal the mechanism underlying transition boiling and provide a comprehensive understanding of the entire boiling curve under a unified, physical framework.

**Author contributions**

N.A.P. and T.Y.Z. conceived and planned the research, performed the analyses, and wrote the manuscript.

**Competing interests**

The authors declare no competing interests.

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