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A local equation of state for a fluid in the presence of a wall and its application to rewetting

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Abstract—The liquid-to-vapor transition that occurs when a liquid comes into contact with a hot wall is considered. Statistical mechanics are used to derive an approximate *local* equation of state for the fluid as a function of distance from the wall and to arrive at a wall rewetting criterion. The contact angle is a convenient parameter characterizing the liquid–solid interaction under these conditions. It is shown that the spinodal temperature is a good estimation for the maximum superheat temperature that a liquid can sustain on a wall for most situations encountered in rewetting experiments.

INTRODUCTION

REWETTING phenomena refer to the transitions between initial heat transfer regimes characterized by a high-temperature and essentially dry wall, to regimes where the wall is predominantly wetted and has a high heat transfer coefficient. These phenomena are important in the analysis of a loss of coolant accident of a nuclear reactor and are also encountered in other industrial applications such as cryogenic processes or filling of liquefied natural gas pipelines. In the simplest case of pool boiling, the initial dry state corresponds to film boiling and the wet state to nucleate boiling. The temperature at which this transition takes place is referred to as the minimum film boiling (MFB) temperature. The term MFB is often used to describe other analogous returns to wetted-wall boiling.

In this work, we define the rewetting temperature as the temperature at which the liquid can touch the wall without being immediately turned into vapor. As defined here, the rewetting temperature is not always equal to the MFB temperature because, in some cases, the latter is determined by other important mechanisms such as a hydrodynamic instability. In order for the rewetting temperature to be equal to the MFB temperature, at least two conditions must be satisfied: (a) the vapor film has to be disrupted by some mechanism and (b) the heat removed by direct contact has to be significantly higher than that removed through the vapor layer.

An early expression for the MFB temperature in pool boiling is due to Berenson [1]; it is based on a Taylor instability of the vapor film separating the hot surface from the liquid. Henry [2] improved this model by taking liquid–solid contacts into account. Such contacts were observed in stable film boiling by Bradfield [3] and studied later by Yao and Henry [4] who showed that conditions (a) and (b) above were met for pool boiling on a stainless steel heater whose dimensions are larger than the Taylor instability wavelength.

Spiegler *et al.* [5] assumed that the rewetting temperature is determined by the maximum superheat temperature of the liquid, T_{MAX}, because above this temperature the liquid would immediately turn into vapor and thus could not touch the surface. Rewetting models based on this maximum superheat temperature hypothesis usually consider that rewetting will not occur if the liquid temperature at the contact point with the solid, T_{INT}, is higher than a maximum temperature at which liquid can exist, T_{MAX}. The rewetting temperature is thus given by

$$T_{\mathrm{INT}}(T_{\mathrm{W}} = T_{\mathrm{REW}}, T_{\mathrm{L}}) = T_{\mathrm{MAX}} \tag{1}$$

where $T_{\mathrm{INT}}(T_{\mathrm{W}}, T_{\mathrm{L}})$ is the temperature at the contact point between a wall and liquid whose temperatures are respectively T_{W} and T_{L}, as shown in Fig. 1.

Spiegler *et al.* [5] assumed that the contact temperature is equal to the wall temperature at some distance from the interface $T_{\mathrm{INT}} = T_{\mathrm{W}}$, and that T_{MAX} is given by the spinodal limit of the van der Waals equation of state for the fluid, which at low pressure is given by $T_{\mathrm{MAX}} = \frac{27}{32} T_{\mathrm{c}}$, where T_{c} is the thermodynamic critical temperature. Lienhard [6] gives the following expression for the maximum superheat:

$$T_{\mathrm{MAX}} = \left[0.905 + 0.095\left(\frac{T_{\mathrm{sat}}}{T_{\mathrm{c}}}\right)^{8}\right] T_{\mathrm{c}} \tag{2}$$

which is based on the spinodal limit of improved

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NOMENCLATURE

A	atomic number
c_p	heat capacity
k	thermal conductivity or Boltzmann constant
p	pressure
r	distance
T	temperature
w	potential
z	distance from wall.

Greek symbols

α	defined by equation (16)
γ	surface tension
ε_w	strength of wall fluid interaction, equation (41)
η	defined by equation (28)
ϑ	contact angle
λ	inverse range parameter, equation (11)
μ	chemical potential
ρ	density
σ	hard sphere diameter
φ	defined by equation (21)
ϕ	potential.

Subscripts

ATT	attractive
c	critical
hs	hard sphere
INT	interface
L	liquid
REP	repulsive
REW	rewetting
sat	saturation
spin	spinodal
V	vapor
W	wall.

equations of state and is valid up to the critical pressure.

The maximum superheat can also be determined by the homogeneous nucleation theory which is reviewed by Blander and Katz [7] and Avedisian [8]. Both the spinodal and homogeneous nucleation theories give similar results for the maximum superheat temperature, as shown by Lienhard and Karimi [9]. The interfacial temperature upon contact can be related to the bulk liquid and wall temperatures by the infinite slab model, which considers that both liquid and solid behave like two semi-infinite slabs of uniform initial temperatures T_L and T_W that are suddenly brought into contact. The contact temperature T_{INT} is given by Carslaw and Jaeger [10]:

$$T_{INT} = \frac{T_{W,\infty} + \xi T_{L,\infty}}{1+\xi} \tag{3}$$

with

$$\xi^2 = \frac{k_L \rho_L c_{pL}}{k_W \rho_W c_{pW}}. \tag{4}$$

Baumeister and Simon [11] considered the transient conduction problem in the wall and proposed the following expression for this contact temperature for Leidenfrost droplets on clean smooth surfaces:

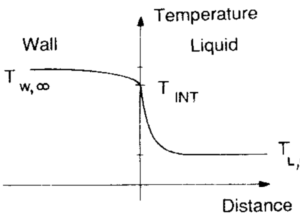

FIG. 1. Temperature distribution in the vicinity of the wall.

$$T_{INT} - T_L = (T_{W,\infty} - T_L) \times \exp(3.06 \times 10^6 \beta) \operatorname{erfc}(1760\sqrt{\beta}) \tag{5}$$

with

$$\beta = (k_W \rho_W c_{pW})^{-1}, \tag{6}$$

calculated in SI units.

The numerical factors were adjusted to fit experimental data. erfc (y) is the complementary error function:

$$\operatorname{erfc}(y) = 1 - \operatorname{erf}(y). \tag{7}$$

These authors also proposed that the maximum superheat is given by

$$T_{MAX} = \frac{27}{32} f T_c \tag{8}$$

where f is an empirical correction factor to the spinodal limit which takes surface effects into account; for pure metals

$$f = 1 - \exp\left[-0.052\left(\frac{(\rho_W/A_W)^{4/3}}{\gamma_{LV}}\right)^{1/3}\right] \tag{9}$$

where A_W is the atomic number of the wall and γ_{LV} the surface tension of the liquid (ρ_W and γ_{LV} in SI units). Segev and Bankoff [12] assumed that the maximum contact temperature is given by the temperature at which a monolayer of adsorbed molecules can exist on the wall. Their results are very sensitive to an arbitrary 'covering' factor.

It is thus seen that surface material effects can be important both in the determination of the interfacial temperature upon contact and in the determination of the maximum possible contact temperature.

In the present work, we consider that the liquid-to-vapor phase transition which occurs when the liquid enters into contact with the very hot wall will usually take place in the first few molecular layers of fluid adjacent to the wall. In these first fluid layers, interfacial phenomena due to intermolecular interactions between the wall and fluid take place. The surface tension is a manifestation of such effects; we further postulate that certain fluid properties in this region are different from bulk fluid properties (see, e.g. Croxton [13]). The scope of this work is to investigate the influence on the rewetting temperature of this interfacial fluid region.

The method adopted is a statistical–mechanical derivation of the equation of state of a fluid, in which the presence of a wall has been taken into account. The fluid is modeled by molecules interacting with each other through a pair potential which contains a hard-sphere repulsive core and a very weak and long range attractive part. For a uniform fluid this modelization leads to a van der Waals type equation of state [14]. The fluid in our case is bounded in one direction by an impenetrable wall which creates a long range attractive potential for the fluid molecules. The inhomogeneity in the fluid which is created by the wall is treated by an approach originally formulated by van Kampen [15]. Introducing suitable approximations, an equation of state is obtained which is dependent on the distance from the wall; the critical temperature and pressure, as well as the spinodal temperature, now depend on the distance from the wall. The local equation of state is then applied to the specific problem of the determination of the maximum superheat temperature of a liquid in the presence of a wall and is compared to experimental data.

The contact angle between a liquid and a solid can be related to the intermolecular potential for a specific choice of potentials, as shown by Sullivan [16]. This is clearly useful for comparing the theory with experimental data, since the contact angle is a convenient parameter characterizing the liquid–solid interaction.

EQUATION OF STATE OF A FLUID CLOSE TO A WALL

Mean field theory

We consider a single-component fluid bounded in one direction by a plane impenetrable wall. The liquid molecules interact with each other with a pairwise additive potential $w^{L}(r)$ which depends only on the distance r between two molecules. This potential is split somewhat arbitrarily into a repulsive component w^{L}_{REP} which will be taken to be identical to a hard-sphere potential, and an attractive component w^{L}_{ATT}:

$$w^{L}(r) = w^{L}_{REP} + w^{L}_{ATT}. \tag{10}$$

The hard-sphere potential corresponds to an infinitely repulsive potential for intermolecular separations $r < \sigma$ and a zero interaction for $r > \sigma$, where σ is the molecular diameter. The attractive component is assumed to be very weak and long ranged. These features can be considered by introducing an inverse range parameter λ in the following form of the attractive potential:

$$w^{L}_{ATT}(r) = \lambda^{3}\Phi(\lambda r). \tag{11}$$

In the formal limit $\lambda \to 0$, the effect of the attractive intermolecular potentials is merely to provide a background potential ϕ^{L} given by ref. [17] as

$$\phi^{L}(z) = \int_{\mathrm{FLUID}} d^{3}\mathbf{r}' w^{L}_{ATT}(|\mathbf{r}-\mathbf{r}'|)\rho(\mathbf{r}') \tag{12}$$

which now acts on a fluid whose molecules have hard-sphere interactions given by w^{L}_{REP}.

In our model, the effect of the wall is to create an additional external potential ϕ^{W} for the fluid molecules which is assumed to depend only on the distance z from the wall, and becomes infinitely positive for $z < 0$ (hard wall). As a consequence, the density $\rho(\mathbf{r}')$ in equation (12) depends only on the distance z' from the wall because the external potential ϕ^{W} is a function of z' only.

The total effective potential $\phi(z)$ acting on a fluid molecule is given by the sum of the liquid–liquid and liquid–wall contributions:

$$\phi(z) = \phi^{L}(z) + \phi^{W}(z). \tag{13}$$

One is now left with the determination of the properties of a hard-sphere fluid (without attractive interactions) in the presence of a total effective external potential $\phi(z)$. In the case of a wall potential $\phi^{W}(z)$ which varies slowly on the scale λ^{-1} and assuming that the density profile $\rho(z)$ is also slowly varying, it can be shown [18] that, in the $\lambda \to 0$ limit, the non-uniform hard-sphere system is determined by the following balance of potentials:

$$\mu = \mu_{\mathrm{hs}}[\rho(z)] + \phi(z) \tag{14}$$

where μ_{hs} is the chemical potential of a hard-sphere fluid at density $\rho(z)$, and $\phi(z)$ is given by equations (12) and (13).

For a fluid of uniform density $\rho(z) = \rho$ of infinite extent in space (no wall) and no imposed potential, $\phi^{W} = 0$, equation (14) can be written in the following form:

$$\mu = \mu_{\mathrm{hs}}(\rho) - \alpha\rho \tag{15}$$

with

$$\alpha = -\int d^{3}\mathbf{r} w^{L}_{ATT}(r). \tag{16}$$

A van der Waals type expression for the pressure p can be derived from equation (15) [14],

$$p = p_{\mathrm{hs}}(\rho) - \tfrac{1}{2}\alpha\rho^{2} \tag{17}$$

where p_{hs} is the pressure of a hard-sphere fluid at density ρ.

Constant density approximation

In order to obtain a local equation of state we consider that the fluid contribution $\phi^{\mathrm{L}}(z)$ to the total mean field $\phi(z)$ in equation (12) can be approximated by taking the fluid density $\rho(z')$ constant over z' at the value $\rho(z)$:

$$\rho(z') = \rho(z). \tag{18}$$

The fluid contribution ϕ_0^{L} which is obtained from equation (12) with this approximation is given by

$$\phi_0^{\mathrm{L}}(z) = \rho(z)\int_{\mathrm{FLUID}} \mathrm{d}^3\mathbf{r}'w_{\mathrm{ATT}}^{\mathrm{L}}(|\mathbf{r}-\mathbf{r}'|). \tag{19}$$

It is clear that the error introduced by this approximation will vanish for a uniform system ($\rho(z)$ constant) for which equation (19) is exactly equivalent to equation (12). The error introduced by the constant density approximation, equation (18), depends on the degree of non-uniformity of the density $\rho(z)$ and is discussed by Gerweck [19]. It improves as the saturation temperature of the system increases, or as the contact angle of the liquid–solid system decreases.

The integral over the liquid region in equation (19) can be written more explicitly by making use of the geometry of the system [19], giving

$$\phi_0^{\mathrm{L}}(z) = -\alpha\varphi(z)\rho(z) \tag{20}$$

with

$$\varphi(z) = \frac{4\pi}{\alpha}\left(\int_0^{\infty} r^2 w_{\mathrm{ATT}}^{\mathrm{L}}(r)\,\mathrm{d}r - \frac{1}{2}\int_z^{\infty} r(r-z)w_{\mathrm{ATT}}^{\mathrm{L}}(r)\,\mathrm{d}r\right) \tag{21}$$

and

$$\alpha = -4\pi\int_0^{\infty} r^2 w_{\mathrm{ATT}}^{\mathrm{L}}(r)\,\mathrm{d}r. \tag{22}$$

Local equation of state

We now consider that at each distance z from the wall, fluid behaves like a hard-sphere fluid of uniform density in the presence of a total external field $\phi_0(z)$ given by equation (13) in which the approximation for the liquid mean field, equation (19), has been introduced. Thus equation (13) becomes

$$\phi_0(z) = \phi_0^{\mathrm{L}}(z)+\phi^{\mathrm{W}}(z). \tag{23}$$

With this approximation, the chemical potential given by equation (14) becomes

$$\mu = \mu_{\mathrm{hs}}[\rho(z)]-\alpha\varphi(z)\rho(z)+\phi^{\mathrm{W}}(z). \tag{24}$$

At the distance z from the wall where the local equation of state is to be determined, we now consider that there is a uniform fluid of density ρ whose total chemical potential is given by equation (24). For this uniform fluid the basic thermodynamic relations can be applied, and the density is related to the pressure and to the chemical potential by the thermodynamic identity

$$\rho = \left(\frac{\partial p}{\partial \mu}\right)\Bigg|_T \tag{25}$$

which leads to a local equation of state relating the density and temperature to the pressure of the fluid at a distance z from the wall [19]:

$$p(\rho, T; z) = p_{\mathrm{hs}}(\rho, T)-\tfrac{1}{2}\alpha\varphi(z)\rho^2 \tag{26}$$

where p_{hs} is the pressure of a uniform hard-sphere fluid at density ρ.

Different choices can be made for the hard-sphere pressure. In the present work, the Carnahan–Starling [20] equation of state is used because it provides an accurate expression for the hard-sphere pressure of a three-dimensional fluid. This hard-sphere pressure is given by

$$p_{\mathrm{hs}} = \rho kT(1+\eta+\eta^2-\eta^3)/(1-\eta)^3 \tag{27}$$

with

$$\eta = \pi\rho\sigma^3/6 \tag{28}$$

where σ is the hard-sphere diameter.

The chemical potential for the hard-sphere expression for the pressure is obtained from the thermodynamic relation

$$\frac{\partial p_{\mathrm{hs}}}{\partial \rho} = \rho\frac{\partial \mu_{\mathrm{hs}}}{\partial \rho} \tag{29}$$

which leads, for the Carnahan–Starling theory, to

$$\mu_{\mathrm{hs}} = kT[\ln(\eta)+\eta(8-9\eta+3\eta^2)/(1-\eta)^3]. \tag{30}$$

We now list the different characteristic properties of the local equation of state, equation (26), as obtained with the Carnahan–Starling hard-sphere theory. The critical ratio, Z_{c}, is given by

$$Z_{\mathrm{c}} = \frac{p_{\mathrm{c}}}{kT_{\mathrm{c}}\rho_{\mathrm{c}}} \cong 0.359 \tag{31}$$

and the critical point of the local equation of state, which according to van der Waals is

$$(p+a\rho^2)(1-b\rho) = \rho kTt,$$

is given as

$$\rho_{\mathrm{c}} = A\sigma^{-3} \tag{32}$$

$$kT_{\mathrm{c}} = \frac{\alpha}{B\sigma^3}\varphi(z) \tag{33}$$

$$p_{\mathrm{c}} = \frac{AZ_{\mathrm{c}}}{B}\frac{\alpha}{\sigma^6}\varphi(z) \tag{34}$$

with $A \cong 0.249$ and $B \cong 11.102$.

It is interesting to note that, independently of the specific choice of intermolecular potentials, we have from equation (21) that $\varphi(z=0) = \frac{1}{2}\varphi(z=\infty)$. Comparing this result with the above expressions for the critical point, equations (32)–(34), we see that the critical temperature and pressure at the wall are half their bulk values, and that the critical density is constant over z. This is due to the vanishing of the wall mean field contribution ϕ^W in the local equation of state, equation (26). Since only fluid–fluid contributions appear in equation (26) and there are no fluid molecules in the space occupied by the wall ($z < 0$), the attractive fluid–fluid potential at the wall, which determines the critical temperature and pressure, is half its bulk value; this gives a critical temperature and pressure at the wall that are half their bulk values.

The maximum superheat temperature (spinodal limit) *at local pressure* p_0 is given by the spinodal condition

$$\left(\frac{\partial p}{\partial \rho}\right)\bigg|_T = 0 \quad \text{at } \rho = \rho_{\text{spin}} \quad \text{and} \quad T = T_{\text{spin}} \tag{35}$$

subject to the condition that the local equation of state, equation (26), relates ρ_{spin} and T_{spin} to the pressure p_0

$$p_0 = p_{\text{hs}}(\rho_{\text{spin}}, T_{\text{spin}}) - \tfrac{1}{2}\alpha\varphi(z)\rho_{\text{spin}}^2. \tag{36}$$

Determination of the density profile and relation with the contact angle

In the limit of infinitely long ranged potentials ϕ^L and ϕ^W and infinitely weak ϕ^L, the density profile $\rho(z)$ is given by the solution of the balance of potentials, equation (14) [21]. This density profile can be solved analytically for a specific choice of intermolecular potentials, as shown by Sullivan [22], and the intermolecular potentials can be related to the contact angle [22]. Since this model is used in the present work, a summary of its relevant results is presented below.

The following choice of intermolecular potentials is made:

$$w_{\text{REP}}^{\text{L}}(r) = +\infty \quad \text{for} \quad r \leqslant \sigma, \tag{37}$$

$$w_{\text{REP}}^{\text{L}}(r) = 0 \quad \text{for} \quad r > \sigma, \tag{38}$$

$$w_{\text{ATT}}^{\text{L}}(r) = -\frac{\alpha}{4\pi}\lambda^3\frac{\exp(-\lambda r)}{\lambda r}, \tag{39}$$

$$\phi^{\text{W}}(z) = +\infty \quad \text{for} \quad z \leqslant 0, \tag{40}$$

$$\phi_{\text{W}}(z) = -\varepsilon_{\text{w}}\exp(-\lambda z) \quad \text{for} \quad z > 0; \tag{41}$$

α is the strength of the fluid–fluid interaction, ε_w the strength of the wall–fluid interaction and λ^{-1} is a typical length which is taken as identical for both interactions. The Yukawa potential for the fluid interaction, equation (39), gives a van der Waals type equation of state in the case of a uniform fluid; the exponential for the wall, equation (41), allows the density profile to be conveniently solved.

Defining $x = \lambda z$ and applying $\mathrm{d}^2/\mathrm{d}z^2$ to equation (14) with these potentials leads to the following results; the details of the derivations are given in ref. [22]:

$$\frac{\mathrm{d}\mu_{\text{hs}}^*}{\mathrm{d}x} = \pm\sqrt{(\Psi(\mu_{\text{hs}}^*))} \tag{42}$$

where

$$\Psi(\mu_{\text{hs}}^*) = (\mu_{\text{hs}} - \mu)^2 - 2\alpha(p_{\text{hs}}^* - p), \tag{43}$$

$$p = p_{\text{hs}}(\rho_\infty) - \tfrac{1}{2}\alpha\rho_\infty^2, \tag{44}$$

$$\rho_\infty = \rho(z \to \infty); \tag{45}$$

p corresponds to the pressure of the fluid at bulk density ρ_∞ and μ_{hs}^*, p_{hs}^* denote the local hard-sphere chemical potential and pressure $\mu_{\text{hs}}[\rho(x)]$, $p_{\text{hs}}[\rho(x)]$.

The boundary conditions at the wall $\phi^W(z) = +\infty$ for $z \leqslant 0$; and $\rho(z) = 0$ for $z < 0$ become

$$\Upsilon[\mu_{\text{hs}}^*(0)] = \pm\sqrt{(\Psi[\mu_{\text{hs}}^*(0)])} \tag{46}$$

where

$$\Upsilon(\mu_{\text{hs}}^*) = \mu_{\text{hs}}^* - \mu - 2\varepsilon_{\text{w}}. \tag{47}$$

Once the dependence of the hard-sphere fluid pressure and chemical potential are specified by an adequate equation of state such as equations (27) and (30), the density at the wall $\rho(0)$ is obtained from equations (42) and (46), while the density profile $\rho(x)$ for $x > 0$ is given by quadrature of equation (42).

In all this discussion the density profile was assumed to vary only over a long range λ^{-1}, however, the abrupt variation in the external potential at the wall creates short range oscillations in this density profile. Sullivan [22] shows that it is consistent to neglect these short range oscillations in the limit $\lambda \to 0$.

Since for most practical applications related to the rewetting phenomena the molecular parameter ε_w is not well known, it is useful to express it in terms of the more accessible contact angle θ. The procedure developed by Sullivan [16] will be used here.

We consider a system in which coexisting liquid and vapor exhibit a contact angle θ on the surface of a solid. This contact angle θ is related to the interfacial tensions by Young's equation:

$$\cos(\theta) = \frac{\gamma_{\text{SV}} - \gamma_{\text{SL}}}{\gamma_{\text{LV}}} \tag{48}$$

where γ_{SV} and γ_{SL} are the interfacial tensions between the solid and the saturated vapor, and the solid and saturated liquid. γ_{LV} is the interfacial tension between coexisting liquid and vapor phases.

The interfacial tension of a non-uniform fluid, in which interfacial inhomogeneities are taken into account, is given by

$$\gamma = \frac{\Omega + pV}{\mathscr{A}} \tag{49}$$

where Ω is the grand potential, p the bulk fluid pressure, V the total volume and $\mathscr{A}$ the interfacial area. The interfacial tension γ_{S} between the solid and vacuum should be added in order to obtain the interfacial tension between the fluid and the solid. However, γ_{S} cancels out in the expression for the con-

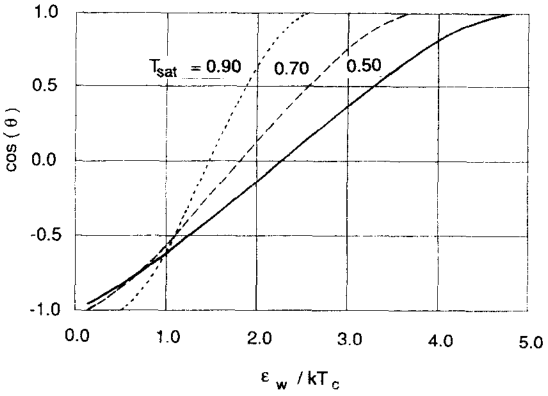

FIG. 2. Relation between the strength of wall–fluid interaction ε_w and contact angle θ at different saturation temperatures.

tact angle, equation (48), and will thus not be introduced here.

By using equation (49) and the fluid–wall model presented in the preceding section, the following expressions for the interfacial tensions are obtained [16]:

$$\gamma_{LV} = \frac{1}{\alpha\lambda}\int_{\mu_{hs,v}}^{\mu_{hs,l}} \sqrt{(\Psi(\mu^*_{hs}))}\,d\mu^*_{hs} \tag{50}$$

$$\gamma_{SV} = \frac{1}{\alpha\lambda}\left\{-\varepsilon_w^2 + \int_{\mu^+_{hs,v}}^{\mu_{hs,v}(0)} \Upsilon(\mu^*_{hs,v})\,d\mu^*_{hs,v} - \int_{\mu^*_{hs,v}(0)}^{\mu_{hs,v}} \sqrt{(\Psi(\mu^*_{hs,v}))}\,d\mu^*_{hs,v}\right\} \tag{51}$$

$$\gamma_{SL} = \frac{1}{\alpha\lambda}\left\{-\varepsilon_w^2 + \int_{\mu^+_{hs,l}}^{\mu_{hs,l}(0)} \Upsilon(\mu^*_{hs,l})\,d\mu^*_{hs,l} + \int_{\mu^*_{hs,l}(0)}^{\mu_{hs,l}} \sqrt{(\Psi(\mu^*_{hs,l}))}\,d\mu^*_{hs,l}\right\} \tag{52}$$

where

$$\Upsilon(\mu^+_h) = 0. \tag{53}$$

The subscripts l and v indicate that the state of the fluid at $x \to \infty$ is either saturated liquid or saturated vapor.

The contact angle can now be related to the strength of the wall–fluid interaction. Numerical results, giving the relation between ε_w and θ, which are based on the solution of equations (48) and (50)–(52) using the Carnahan–Starling equation of state, are shown in Fig. 2.

APPLICATION TO REWETTING

Using the specific choice of potentials introduced above (equations (37)–(41)), the local equation of state (26) becomes

$$p(\rho, T; x) = p_{hs}(\rho, T) - \tfrac{1}{2}\alpha\varphi(x)\rho^2 \tag{54}$$

$$\varphi(x) = 1 - \tfrac{1}{2}\exp(-x). \tag{55}$$

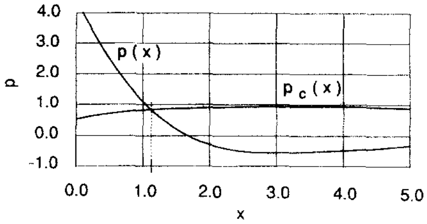

FIG. 3. Typical pressure profile in the fluid.

The critical temperature and pressure, which are dependent on the distance from the wall x, are obtained from equations (33) and (34), which give

$$\frac{T_c(x)}{T_{c,bulk}} = \frac{p_c(x)}{p_{c,bulk}} = \varphi(x). \tag{56}$$

The critical density is constant:

$$\rho_c(x) \equiv \rho_{c,bulk}. \tag{57}$$

We now have a situation in which the thermodynamic properties such as T_c and p_c are dependent on the distance from the wall, as is the pressure $p(x)$ in the fluid. This local pressure $p(x)$ is obtained by solving the density profile $\rho(x)$ as described in the preceding section and introducing this density in the local equation of state (54).

The local spinodal temperature at the distance x from the wall is obtained by considering that the fluid at x is under the local pressure $p(x)$ and by computing the corresponding spinodal temperature $T_{spin}(x)$ as given by equations (35) and (36) for the local pressure $p_0 = p(x)$.

Figure 3 shows a typical pressure profile in which we observe a region close to the wall where the pressure exceeds the local critical pressure, indicating a fluid in a supercritical state. This region is followed by a zone of undercritical pressures, and in some cases the pressure becomes negative over a certain range of distances x from the wall, indicating that the fluid is under tension at these locations. Liquids under negative pressures have been experimentally observed (see e.g. Skripov [23]) and the spinodal limit can be extended in this negative pressure region [22]. Liquids under negative pressure correspond to metastable states if the system temperature is below the corresponding spinodal temperature; these liquids are in an unstable state if the temperature is above the corresponding spinodal limit. At large distances x from the wall, the pressure eventually reaches the bulk saturation pressure.

The point x_0, where the local pressure is equal to the local critical pressure, is defined by

$$p[\rho(x_0); x_0] = p_c(x_0) \tag{58}$$

and in the region $0 < x < x_0$ the fluid is at supercritical pressures.

When the fluid comes into contact with a hot wall, a temperature profile penetrates the fluid, as shown in Fig. 4. This highly transient situation is clearly extremely complex to analyze exactly since it depends on the specific boundary conditions imposed on the temperature and heat fluxes, and it would require the specification of the characteristic length λ^{-1} in order to be completed. However, it is possible to obtain an insight into the effect of the superposition of a temperature profile in a form which can be applied to a rewetting situation, by making the zero-order approximation that the temperature profile does not modify significantly the value of the density profile. This approximation is clearly not valid as soon as a phase transition takes place, since in that case there are indeed important variations in the density profile. However, before the phase transition occurs we assume that the liquid density varies only slightly under the effect of the temperature profile.

We thus consider that the temperature profile is applied on a fluid whose thermodynamic properties, especially the critical and spinodal temperatures, are the same as for the corresponding saturated system. Depending on the value of the interfacial temperature $T_{\rm INT}$ at $x = 0$ and the fluid–wall situation, different mechanisms for the phase transition will take place, which are now discussed.

The creation of a vapor layer between wall and solid can occur either through spinodal decomposition (unstable regime) or nucleation of a stable bubble (metastable regime). We will see that the former usually requires that the temperature profile develops significantly at distances of the order of x_0 from the wall, while the latter requires a penetration distance of the order of the diameter of a stable bubble. The thickness x_0 is of the same order as λ^{-1}, which is of the order of a few molecular diameters, i.e. a few ångstroms. Since the thickness x_0 of the supercritical layer is generally much smaller than the diameter of a stable bubble, the time lapse before vaporization is expected to be much shorter in the unstable regime than in the metastable regime. It is clear that the heat removed during a short contact, all other things being constant, will be less than for a long contact and the same argument that leads to the use of the bulk maximum superheat temperature in the determination of the rewetting temperature is now invoked to postulate that rewetting is not expected if the phase transition occurs through the unstable regime.

Concentrating our attention on whether the superposition of a temperature profile will lead to unstable or metastable regimes, we are led to the conclusion that when the interface temperature is higher than the minimum value over x of the spinodal temperature, there will be an unstable regime. In that case, the liquid will be vaporized extremely quickly and thus rewetting of the surface is not expected. *We define thus the interfacial rewetting temperature as the minimum value of the local spinodal temperature for all distances from the wall*:

$$T_{\rm INT,REW} = {\rm Min}\,[T_{\rm spin}(x)]. \qquad (59)$$

One should bear in mind that for rewetting to actually occur, the contacts that may potentially lead to rewetting must be created by some perturbation of the vapor film. The rewetting temperature as given by equation (59) is thus a limit above which rewetting is not expected to occur.

The results presented above can be summarized by introducing a factor f relating the bulk critical temperature T_c of the fluid to the interfacial rewetting temperature $T_{\rm INT,REW}$

$$T_{\rm INT,REW} = fT_c \qquad (60)$$

with

$$f = {\rm Min}\,[T_{\rm spin}(x)]/T_c. \qquad (61)$$

The values of the factor f for different ε_w/kT_c and $T_{\rm sat}$, obtained numerically, are shown in Fig. 5.

For a system at a given pressure p_0, this factor f has values ranging from the reduced saturation temperature $T_{\rm sat}(p_0)/T_c$ at low surface wettings (low values of ε_w/kT_c) up to values equal to the reduced bulk spinodal temperature $T_{\rm spin}(p_0)/T_c$ for well wetting surfaces (high values of ε_w/kT_c). The saturation values which are obtained at low ε_w/kT_c correspond to a situation in which the liquid is almost in the presence of a free surface created by the wall, since the low interaction with the wall molecules becomes similar to the low interaction with the vapor. It is thus not surprising to see the phase transition occurring as soon as the saturation temperature is reached, as would be the case for a fluid in the presence of a free surface. For high values of ε_w/kT_c this factor f becomes equal to the bulk spinodal temperature at pressure p_0, as obtained from a classical mean-

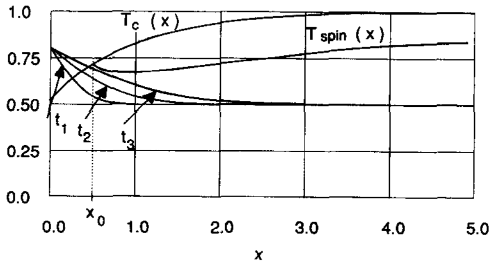

FIG. 4. A temperature profile penetrating the fluid.

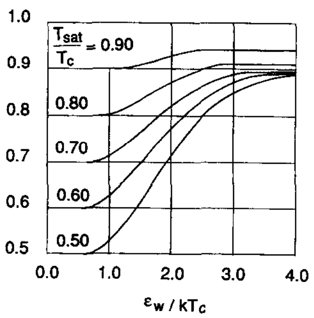

FIG. 5. Values of the factor f for different ε_w/kT_c and $T_{\rm sat}/T_c$ values.

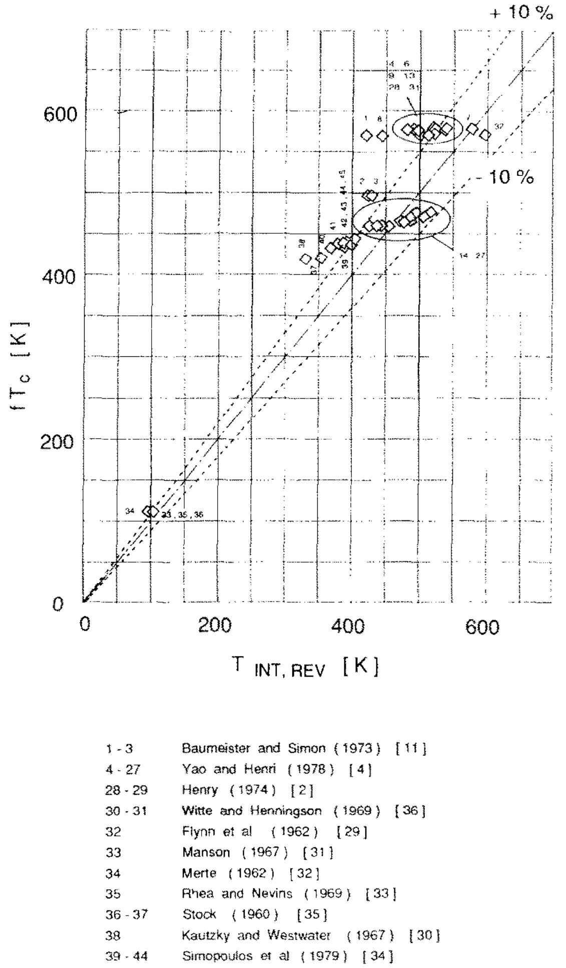

FIG. 6. Comparison with experimental data.

field equation of state using the Carnahan–Starling expression for the hard-sphere contribution.

A comparison between experimental data for the interfacial contact temperature at rewetting $T_{\mathrm{INT,REW}}$ and the predicted value fT_c is shown in Fig. 6. The interfacial rewetting temperature has been obtained from minimum (essentially pool) film boiling and Leidenfrost temperature data. The data used here cover a large number of fluid/surface combinations in order to provide a good assessment of the theoretical results. The majority of the points lie in a $\pm 10\%$ range from the predicted values and the significant deviations are in the direction of an actual rewetting temperature which is lower than predicted. This can be explained by the fact that the present model assumes that conditions (a) and (b) of the Introduction are met, which is not always the case. For example, if there are not enough perturbations of the vapor film, the rewetting temperature can be very low, as is found in the so-called metastable film boiling situation where film boiling over an extremely smooth surface is sustained down to temperatures close to saturation.

DISCUSSION

Range of intermolecular forces

Within the present model, the range of intermolecular forces λ^{-1} can be obtained by fitting combinations of contact angle data and liquid–vapor surface tension data [16]. Values for λ^{-1} of the order σ, which is generally a few ångstroms, are obtained. This is in apparent contradiction with the requirement that there should be many molecules in the perturbed fluid layer, whose thickness is of the order of λ^{-1}. Actually there are indeed many molecules in this layer because one has to consider not only the direction normal to the interface: there are an infinite number of molecules in the directions parallel to the interface. Moreover, by using a spinodal criterion for the maximum superheat, there is no minimum size requirement for the phase transition to occur, such as a critical radius for homogeneous nucleation. Eventually, we note that the interfacial density change of a free liquid–vapor surface takes place over a very small distance of the order of σ, and that this surface affects the whole behavior of the bulk fluid, bringing the phase transition temperature to T_{sat}, while without such an interface, the phase transition occurs at the higher temperature T_{spin}.

Surface contamination

We now investigate the effect of surface contamination of the factor f. Surface contamination usually increases the contact angle θ [24], which means that the parameter ε_w/kT_c describing the wall–surface interaction decreases. At first sight, the effect of surface contamination will thus be a reduction of the factor f, which implies a reduction of the rewetting temperature. However, the experimental data show that surface contamination increases the rewetting temperature [11, 25]. This apparently contradictory result is explained by two reasons which are now discussed.

It must first be recognized that one of the features of a contaminated surface is the existence of an oxide layer which has a low value of the coefficient $\sqrt{(k\rho c_p)}$. Consequently, the interfacial temperature upon contact will be lower than for a less contaminated surface which has a thinner or no oxide layer, allowing a higher rewetting temperature. This aspect of surface contamination is able to explain the increase of the rewetting temperature, as shown by Moreaux *et al.* [26]. Along with this effect which increases the rewetting temperature, a contamination of the surface is usually not expected to lead to a significant variation of the factor f. Indeed, by considering the experimental rewetting situation of water on a metallic surface at atmospheric pressure, we have for a clean surface a low contact angle $\theta \cong 0$ which implies a liquid–solid interaction, $\varepsilon_w/kT_c \cong 5$. At atmospheric pressure the corresponding factor is $f = 0.89$. For the same situation, a contaminated surface with a contact angle $\theta \cong 45°$, which implies $\varepsilon_w/kT_c \cong 4$, will still have the same factor $f = 0.89$.

Even for a contact angle of 60° the variation of the factor f is less than 1%. We conclude that *surface contamination will usually have a negligible effect on the factor f*; whereas because of the thermal resistance due to contamination (i.e. the reduced value of k_w on the surface), the contact temperature, equation (3), is reduced, which in turn implies a higher rewetting temperature, as is observed in the experiments.

Coating with poorly wetting materials

For a Teflon-coated surface, or a surface coated with silicon grease, Gaertner [27] reports a qualitative decrease in the minimum film boiling temperature of water. These surfaces have a contact angle of approximately $\theta = 108°$ from which a factor $f = 0.72$ is obtained instead of the bulk value $f = 0.89$. This corresponds to an important (19%) decrease of the minimum film boiling temperature with respect to a surface which has a low contact angle $\theta \cong 0$; which is in agreement with the qualitative observations made by Moreaux *et al.* [26].

Liquid metals

Liquid metals usually have a rewetting temperature which is lower than the one which would be obtained from the bulk spinodal temperature [11, 28]. This may be partially due to the deviation of liquid metals from the conventional equations of state used to determine the spinodal limit [27]. The theory which is developed in the present work explains this deviation qualitatively, but fails to give an accurate quantitative prediction for the rewetting temperature. This is because, unfortunately, liquid metals fall in the region where the local density approximation, which was made in order to derive the local equation of state, becomes too crude, as shown below.

A numerical example can be taken for mercury which has a contact angle of approximately $\theta \cong 140°$ on most metallic surfaces [23]. With a critical temperature for mercury of $T_c = 1735$ K, the isotherm for the determination of the fluid–wall interaction ε_w/kT_c is $293/1735 = 0.17$. This gives a value of $\varepsilon_w/kT_c = 0.5$. However, these values of the parameters are in a region where the local density approximation is not accurate, as shown in ref. [19], because of the relatively large density gradient that occurs in this case. The isotherm for the determination of the factor f is $630/1735 = 0.36$, where 630 K is the saturation temperature of mercury at atmospheric pressure. The corresponding factor for $\varepsilon_w/kT_c = 0.5$ is $f = 0.36$, which implies a rewetting temperature equal to the saturation temperature $T_{\mathrm{INT,REW}} = 630$ K, whereas experimental rewetting data are in the range of 811–950 K [11]. We conclude that the qualitative trend for liquid metals is predicted by the theory, but that an accurate prediction of the rewetting value is not possible with the present theory because liquid metals are in a region where the constant approximation inherent to this theory is not accurate.

CONCLUSION

A local equation of state for a fluid in the presence of a wall has been developed. Applying this theory to the rewetting situation, it was shown that the bulk spinodal temperature is a good estimation of the maximum superheat temperature of a liquid at a wall for most liquid–wall situations encountered in rewetting experiments. This is due to the low value of the contact angle which characterizes the most common rewetting situations.

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UNE EQUATION D'ETAT LOCALE D'UN FLUIDE EN PRESENCE D'UNE PAROI ET SON APPLICATION AU REMOUILLAGE

Résumé—On considère la transition liquide–vapeur qui se produit lorsqu'un liquide entre en contact avec une paroi surchauffée. Une équation d'état du fluide *locale*, fonction de la distance à la paroi, est obtenue (moyennant certaines approximations) à partir de considérations de mécanique statistique. L'angle de contact s'avère être un paramètre utile pour caractériser l'interaction liquide–paroi. On montre que pour la plupart des situations de remouillage, la température limite de stabilité du liquide homogène reste proche de la température maximale supportable par le liquide en contact avec la paroi.

EINE ÖRTLICHE ZUSTANDSGLEICHUNG FÜR EIN FLUID AN EINER WAND UND IHRE ANWENDUNG AUF WIEDERBENETZUNGSVORGÄNGE

Zusammenfassung—Es wird der Phasenwechsel eines Fluides von flüssig nach dampfförmig bei Berührung mit einer heißen Wand betrachtet. Mit Hilfe statistischer Methoden wird eine angenäherte örtliche Zustandsgleichung für das Fluid als Funktion des Wandabstandes ermittelt. Daraus ergibt sich ein Kriterium für die Wiederbenetzung. Der Benetzungswinkel ist ein geeigneter Parameter zur Beschreibung der Wechselwirkung zwischen Wand und Fluid bei derartigen Bedingungen. Es zeigt sich, daß die Spinodalen-Temperatur ein guter Näherungswert für die maximale Überhitzungstemperatur ist, die ein Fluid an der Wand erreichen kann. Dies ergibt sich aus fast allen Wiederbenetzungsexperimenten.

ЛОКАЛЬНОЕ УРАВНЕНИЕ СОСТОЯНИЯ ЖИДКОСТИ У СТЕНКИ И ЕГО ПРИМЕНЕНИЕ К СЛУЧАЮ ПОВТОРНОГО СМАЧИВАНИЯ

Аннотация—Рассматривается проблема перехода от жидкости к пару при контакте жидкости с горячей стенкой. Вывод приближенного локального уравнения состояния жидкости как функции расстояния от стенки проводится на основе статистической механики, в результате чего получен критерий повторного смачивания поверхности. Удобным параметром, характеризующим взаимодействие между жидкостью и твердым телом в этих условиях, является угол смачивания. Показано, что с помощью спинодальной температуры можно получить хорошую оценку максимальной температуры перегрева жидкости на стенке для большинства случаев, встречающихся в экспериментах по повторному смачиванию.