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LETTER TO THE EDITOR

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Abstract. The diffusional growth of wetting droplets on the boundary wall of a semi-infinite system is considered in different regions of a first-order wetting phase diagram. In a quasistationary approximation of the concentration field, a general growth equation is established on the basis of a generalized Gibbs–Thomson relation which includes the van der Waals interaction between the droplet and the wall. Asymptotic scaling solutions of these equations are found in the partial-, complete-, and pre-wetting regimes.

The physics of wetting phenomena has attracted much interest in recent years, both from experimental [1–3] and from theoretical [4–9] points of view. Whereas initially static properties dominated the discussion, the interest has shifted more recently to the dynamics of wetting [6, 10–17]. In many experimental situations the formation of a wetting layer starts with the nucleation of droplets on the boundary wall of the system. The central question therefore is that of the temporal evolution of the droplet profile.

There are essentially two different types of dynamic behaviour of a liquid surface droplet. The first is a spreading process which e.g. dominates if a droplet of a non-volatile liquid is overheated from below to above a wetting transition point. Such processes are driven by hydrodynamic modes of the liquid, and they have been discussed extensively in the literature [6, 10–12]. The second mechanism is the phase transformation (condensation or evaporation) between the liquid and the vapour phase of the droplet. This is driven by particle diffusion in the vapour, and e.g. is the dominating process in the growth of supercritical droplets in a metastable situation.

Whereas the diffusional growth of a homogeneous wetting layer has been discussed in the literature [16], this seems not to be the case for surface droplets. The present contribution deals with the diffusional growth of a supercritical droplet from a supersaturated vapour. This process is accompanied by the creation of latent heat, and it will be assumed that heat transport as well as other hydrodynamic modes are fast compared to the diffusion. As a consequence the droplet is isothermal and always has a shape which minimizes its free energy at a given volume. The time dependence of this shape is the main object of interest in this work.

The excess free energy of a wetting film of local thickness $f(x)$ on a planar boundary wall of a semi-infinite system can be written in the form [18, 19]

$$\mathcal{H}_h[f] = \int \mathrm{d}^2x \left[\frac{\gamma}{2} (\boldsymbol{\nabla} f)^2 + V(f) - hf \right] \tag{1}$$

where γ is the interface stiffness, h is the difference of the chemical potential from that of the saturated vapour, and $V(f)$ is an effective interface potential. The field h can be expressed as

the difference between the vapour concentration c and its value c_0 at saturation, so in linear order

$$c = c_0(1 + \Gamma h). \tag{2}$$

The form of the potential $V(f)$ corresponding to a first-order wetting transition is sketched in figure 1. There, for temperatures T less than the wetting temperature T_w, the global minimum of $V(f)$ is at $f = f_0$, whereas for $T > T_w$ this minimum becomes metastable in favour of the global minimum at diverging film thickness. For $f \to \infty$ we assume $V \propto f^{1-\sigma}$, where $\sigma = 3$ for non-retarded and $\sigma = 4$ for retarded van der Waals interactions [6].
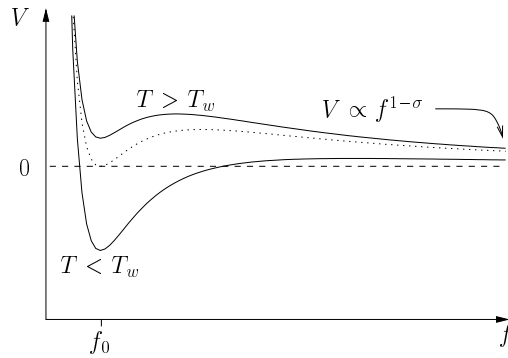
Figure 1. A sketch of an effective interface potential that shows a first-order wetting transition as T is raised from $T < T_w$ to $T > T_w$.

Homogeneous (i.e. $f(x) = $ constant) minima of the excess free energy $\mathcal{H}_h[f]$ (i.e. the *global* minima of $V(f) - hf$) determine the phase diagram, shown in figure 2. In the region $h > 0$, where the liquid bulk phase is stable, a film of infinite thickness forms on the wall in thermal equilibrium. On the line $h = 0$, which means bulk coexistence of the liquid and vapour phases, the first-order wetting transition occurs at $T = T_w$, where $f = f_0$ for $h = -0$, $T < T_w$ (partial wetting), and $f = \infty$ for $T > T_w$ (complete wetting). From the transition point a pre-wetting line $h_p(T)$ extends into the region $h < 0$ where the vapour phase is stable in the bulk. This line separates a region (below $h_p(T)$) where the wall is covered by a thin film from a region ($h > h_p(T)$) where the wall is covered by a thick film. The jump in film thickness along the pre-wetting line vanishes at the pre-wetting critical point T_{pw}. The partial-wetting line $h = 0$, $T < T_w$ and the pre-wetting line $h_p(T)$ together form a first-order line as regards the wetting properties of the system [21].

If the system is quenched from below to above the first-order line (for example by increasing the pressure), the phase transition is initialized by the formation of critical droplets on the wall (provided that one stays within the surface spinodal lines, shown in figure 2). The shape of these critical droplets is qualitatively different in different regions of the phase diagram [22–24]. Axisymmetric profiles $f(r)$ can be calculated via the saddle-point equation

$$\delta\mathcal{H}_h/\delta f(r) = 0 \tag{3}$$

with the natural boundary conditions of a droplet profile

$$f'(0) = 0 \qquad \lim_{r \to \infty} f(r) = f_0. \tag{4}$$

As illustrated in figure 2, this leads to spherical (in the squared-gradient approximation of equation (1), parabolic) caps in the partial-wetting regime, to flat cylindrical droplets (pancakes) in the pre-wetting regime [6], and to ellipsoid-like droplets in the complete-wetting regime [22].
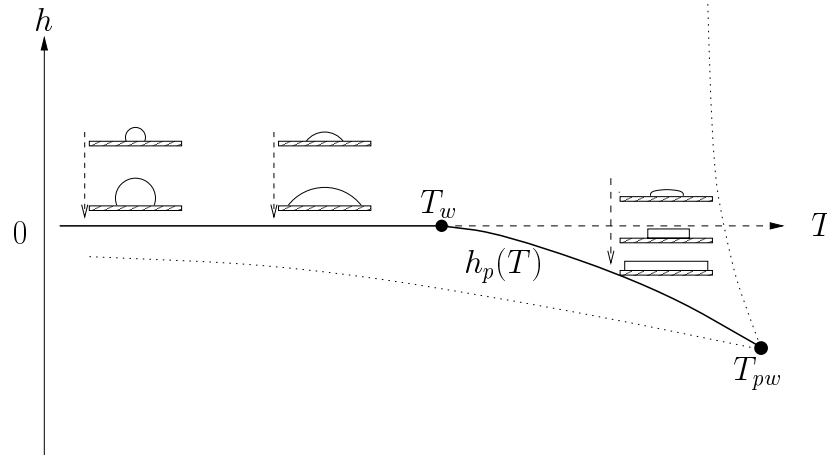
Figure 2. The wetting phase diagram: the first-order line of wetting transitions consisting of the partial-wetting line $h = 0$, $T < T_w$ and the pre-wetting line $h = h_p(T)$ is marked by a solid line. The different types of growing wetting droplets along isotherms are shown in the different regions of the phase diagram. The dotted lines refer to the surface spinodals which enclose the nucleation regime.

The saddle point $\delta\mathcal{H}_h/\delta f(r) = 0$ has an unstable growth mode, but the volume-preserving shape fluctuations are stable [23, 24].

Assuming that the volume growth of the droplet is slow, the diffusion in the surrounding concentration field c becomes quasistationary and can be approximated by the Laplace equation

$$D\,\Delta c = 0 \tag{5}$$

where D is the diffusion constant. At long distances from the droplet, the concentration field is given by the system concentration $c_\infty(t)$ which is time dependent in a supersaturated system ($h > 0$) because of the phase-separation process in the metastable bulk phase. The normal derivative of the concentration field on the boundary wall of the system vanishes because there is no diffusion flux into the wall, i.e. the Neumann boundary condition

$$D\,\partial_\perp c\big|_{\text{wall}} = 0 \tag{6}$$

has to be fulfilled.

To obtain a well defined diffusion problem, the boundary condition on the surface as well as the actual shape of the supercritical droplet need to be specified. In view of the slow diffusional growth of the droplet, the concentration field close to the droplet surface is assumed to be in local thermal equilibrium. Therefore the local chemical potential $h(x)$ at the droplet surface is given by $h(x) = \delta\mathcal{H}_0/\delta f(x)$ which due to (2) corresponds to a concentration

$$c_s(x) = c_0\left(1 + \Gamma\frac{\delta\mathcal{H}_0}{\delta f(x)}\right) \tag{7}$$

which can be denoted as a generalized Gibbs–Thomson relation for wetting droplets. The expression $\delta\mathcal{H}_0/\delta f$ consists of a term γ times the local curvature K of the droplet interface plus an interaction term $\partial V/\partial f$. Neglect of the interaction term reduces (7) to the classical Gibbs–Thomson relation $c_s = c_0(1 + \Lambda K)$ with the capillary length $\Lambda \equiv \Gamma\gamma$. It identifies the concentration at a curved interface as the concentration c_0 for a flat interface modified by a linear curvature correction.

The assumption of fast hydrodynamic modes (compared with the diffusional growth) implies that the shape of a growing droplet can be calculated by minimizing its free energy under the constraint of a fixed droplet volume $\Omega(t)$. Technically, this variational calculation leads again to equation (3) with the boundary conditions (4) but now with the chemical potential h in (3) replaced by a function $h_{\Omega(t)}$ which includes a Lagrange parameter corresponding to $\Omega(t)$. Consequently the growing supercritical droplet always looks like a critical droplet at a different time-dependent chemical potential. With increasing volume $\Omega(t)$ the corresponding field $h_{\Omega(t)}$ approaches the first-order line, where eventually the volume of the droplet diverges. In this sense, wetting droplets grow along isotherms towards the first-order line, as illustrated in figure 2.

The saddle-point equation (3) with the fixed-volume constraint is equivalent to $\delta\mathcal{H}_0/\delta f = h_{\Omega(t)}$. Via equation (7), this implies that the Dirichlet boundary condition of the constrained equilibrium droplet is given by

$$c_s(t) = c_0(1 + \Gamma h_{\Omega(t)}) \qquad (8)$$

and therefore independent of x. Especially in the complete-wetting or pre-wetting case, where the droplets are not spherical, one would expect a non-trivial boundary condition having the classical Gibbs–Thomson condition in mind. Additionally, corrections due to the potential $V(f)$, which determine the shape of the droplets in these regions, have to be taken into account. Nevertheless the two effects add up such that equation (7) can be written as equation (8) for a droplet in a volume-constraint equilibrium showing that c_s is constant along the droplet surface!

Now, the x-independent Dirichlet boundary condition (8) allows one to use an electrostatic analogy to solve the quasistationary diffusion problem (5)–(7) for the growing droplet [28]. To fulfil the Neumann condition (6), the system (including the droplet) is mirrored at the boundary wall of the system. Then the field $4\pi Dc$ is identified with an electric potential which also obeys the Laplace equation. The normal derivative of the field, i.e. the diffusion flux density on the droplet surface field, corresponds to the charge density of a conductor with the shape of the droplet including its mirror image. Consequently, the total volume growth of the droplet corresponds to the total charge, which is given by the capacity C of the conductor times the potential difference between the surface and infinity. This ultimately leads to the droplet growth equation

$$\dot{\Omega} = 4\pi DC(t)[c_\infty(t) - c_s(t)] = 4\pi D\Gamma C(t)[h(t) - h_{\Omega(t)}] \qquad (9)$$

where C depends on the droplet profile and therefore is implicitly time dependent [20]. The difference $h(t) - h_{\Omega(t)}$ may be interpreted as the supersaturation of the system with respect to the droplet.

Equation (9), together with equations (1), (3), and (4), allows one to determine self-consistently the growing droplet profile if $h(t)$ is known. For a given volume Ω, the droplet profile can be calculated from equations (1), (3), and (4) with a conveniently chosen Lagrange multiplier h_Ω. Then the capacity C of the conductor represented by the droplet plus its mirror image is calculated. Insertion of C, h_Ω, and the chemical potential h into equation (9) yields the droplet growth rate $\dot{\Omega}(t)$, and integration of (9) eventually determines $\Omega(t)$.

In practice, for large droplets, the calculation can be facilitated by the use of scaling properties of critical droplets close to the first-order transition line [22, 23]. At temperatures $T > T_w$ the wetting droplets on the wall nucleate either as ellipsoid-like droplets at $h \geqslant 0$ (complete wetting) or as pancake-like droplets at $h_p(T) < h < 0$ (pre-wetting). In both cases the droplets grow along an isotherm towards the pre-wetting line ($h_{\Omega(t\to\infty)} \to h_p(T)$). This means that they eventually become pancake-like droplets with a constant height but diverging radius $R(t)$, so the capacity of large droplets is given by the capacity of a flat disc $C(t) \propto R(t)$. In the case where the initial quench leads to a supersaturated bulk system ($h > 0$) the volume

will phase separate until it reaches $h = 0$, whereas for initial values $h < 0$ the vapour bulk phase is stable and h remains constant over time. In either situation the difference $h - h_\Omega$ approaches a non-vanishing constant, so equation (9) yields $\dot{\Omega} \propto \Omega^{1/2}$ or $\Omega \propto t^2$ which implies

$$R \propto t \qquad (10)$$

and is only determined by the time-dependent capacity, i.e. the increasing diffusive coupling to the environment. This fast radial growth may raise some doubts about the validity of the quasistationary approximation (5). A check of self-consistency, i.e. insertion of the quasistationary solution into the complete diffusion equation, shows that the growth exponent 1 in equation (10) is just where the $\partial_t c$ in the diffusion equation becomes marginal in the sense that it approaches a constant instead of vanishing in the late-time behaviour. This constant is proportional to the density ratio of the droplet fluid and the surrounding gas. Since this ratio is usually small, the range of validity of the quasistationary approximation should just include our result.

Wetting droplets at $T = T_w$ in a supersaturated system ($h > 0$) are not spherical, also. Their radius R scales as $R \propto h_\Omega^{-(\sigma+1)/2\sigma}$, their central height F as $F \propto h_\Omega^{-1/\sigma}$, and consequently their volume as $\Omega \propto h_\Omega^{-(\sigma+2)/\sigma}$ [22]. Therefore, the profile of a growing wetting droplet becomes flatter and approaches a disc with capacity $C \propto R \propto h_\Omega^{-(\sigma+1)/2\sigma}$. In a supersaturated system (i.e. $h > 0$) there are not only wetting droplets on the wall, but also droplets in the bulk. The set of growing bulk droplets reduces the supersaturation in a Lifshitz–Slyozov–Wagner-type way as $h \propto t^{-1/3}$ [25–27]. With this input the wetting droplet growth equation (9) can be written as

$$\dot{h}_\Omega h_\Omega^{-2(\sigma+1)/\sigma} \propto h_\Omega^{-(\sigma+1)/(2\sigma)}[At^{-1/3} - h_\Omega] \qquad (11)$$

for large droplets. This leads to the asymptotic growth law $h_\Omega \propto t^{-4\sigma/[3(\sigma+3)]}$ which due to the above scaling properties for R and F implies

$$R \propto t^{2(\sigma+1)/[3(\sigma+3)]} \qquad F \propto t^{4/[3(\sigma+3)]}. \qquad (12)$$

Finally, in the partial-wetting regime $T < T_w, h > 0$, the wetting droplets are spherical caps, and therefore their growth properties are similar to those of bulk droplets, i.e.

$$R \propto t^{1/3}. \qquad (13)$$

The evaluation of the difference $h - h_\Omega$ in equation (9) can only be done in a theory where diffusional interactions between surface and bulk droplets are taken into account [28]. At late stages, partial-wetting droplets in systems at a temperature corresponding to a contact angle $\Theta > \pi/2$ will shrink because $h - h_\Omega$ turns negative for each droplet, whereas droplets at a temperature with $\Theta < \pi/2$ will grow.

The results given in this contribution apply to the intermediate time well after the nucleation period and way before coalescence takes place. This ensures first that a quasistationary description including the scaling properties of the droplet shapes can be used and second that a single-droplet picture is applicable. When the system crosses over to the regime where coalescence becomes dominant, droplet–droplet interactions have to be taken into account and the growth of the closed wetting layer has to be discussed, finally (see e.g. [16]).

One of the basic ingredients of the present calculation is the Neumann boundary condition (6). It derives from the fact that there is no diffusion flux through the wall. Even if the wall is locally in a non-wet state, it is always covered by a film of microscopic thickness f_0. If equation (6) were to be invalid somewhere in such a region, the film would thicken there and the interface would move out of the microscopic minimum of the interface potential shown in figure 1. According to the generalized Gibbs–Thomson relation (7), which includes a term

$\partial V/\partial f$, the local concentration on top of the surface would then increase and the film would evaporate until it reaches the former height f_0 again. Thus, up to fluctuations, equation (6) will be valid.

The calculation of the supercritical droplet shape is based on the assumption of fast hydrodynamic modes compared to the droplet diffusional growth. This assumption may become questionable if a pre-wetting droplet becomes very large. However, at this very late stage the coalescence of different droplets will be dominant anyway.

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