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Recent progress in the moving contact line problem: a review

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Abstract

As pointed out long ago by Laplace, viscosity may become a large perturbation to capillary phenomena, especially close to solid surfaces where molecules may stick. A spectacular consequence of this is the impossibility for a triple line to move on a solid if the liquid/vapor interface is considered as a material surface and if the usual no slip boundary condition is enforced. As shown recently this specific phenomenon of contact line motion can be described by coupled van der Waals and fluid equations, yielding a rational theory that is divergence free and consistent with the equilibrium results. Far from the triple line, the equations of fluid mechanics are recovered in their usual form. In this approach, the contact line move close to the solid by evaporation or condensation, which requires (for evaporation) the molecules to jump above a high potential barrier on their way from the liquid to the vapor. An Arrhenius factor makes this process intrinsically slow, compared to molecular speeds. For (realistic) very small Arrhenius factors, the motion of the triple line induces a dynamical change of the functions in the van der Waals equations. This may lead to dynamical wetting and dewetting transitions, that is, to a change of the contact angle from a finite to a zero value or conversely. The dynamical wetting transition has been observed in liquids flowing down a plate (see Blake and Ruschak, *Nature* 282 (1979) 489–491) cusps on the contact line appear when it recedes faster than the speed of transition. Similar ideas account well also for the known sensitivity of contact line mobility to vapor pressure. *To cite this article: Y. Pomeau, C. R. Mecanique 330 (2002) 207–222.* © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

computational fluid mechanics / moving contact line / phase field / kinetic retardation

Progrès récents sur la ligne de contact mobile : une revue

Résumé

Comme remarqué il y a longtemps par Laplace, la viscosité peut devenir une source de perturbation importante aux phénomènes capillaires, particulièrement près des surfaces solides auxquelles les particules fluides adhèrent. Une conséquence spectaculaire en est l'impossibilité pour la ligne triple de bouger sur un solide si l'on considère l'interface liquide/vapeur comme une surface matérielle et qu'on impose la condition de non glissement des fluides sur le solide. On a montré récemment que ce phénomène spécifique de mouvement de la ligne de contact peut être décrit en couplant les équations de van der Waals et fluides, ce qui conduit à une théorie rationnelle sans divergence et qui reste cohérente avec les résultats de l'équilibre (sans mouvement). Loin de la ligne triple, les équations de la mécanique des fluides s'appliquent sous leur forme habituelle. Dans

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cette approche, la ligne de contact mobile se déplace près du solide par évaporation ou par condensation de vapeur, ce qui, dans le cas de l'évaporation, implique que les molécules passent du liquide à la vapeur en franchissant une barrière de potentiel élevée. Un facteur d'Arrhenius rend donc ce processus intrinsèquement lent, comparé aux vitesses moléculaires. Pour des facteurs d'Arrhenius faibles (et réalistes) le mouvement de la ligne de contact induit un changement dynamique des fonctions entrant dans la théorie de van der Waals. Ce qui peut conduire à une transition de mouillage ou de démouillage, soit à un passage pour l'angle de contact d'une valeur finie à zéro ou réciproquement. La transition de mouillage dynamique a été observée pour des lames liquides descendant sur une plaque (voir Blake et Ruschak, *Nature* 282 (1979) 489–491) : des pointes apparaissent sur cette ligne quand le liquide se retire à une vitesse supérieure à la vitesse de transition. Des idées proches permettent de comprendre la sensibilité connue de la mobilité de la ligne de contact à la tension de vapeur. *Pour citer cet article : Y. Pomeau, C. R. Mécanique 330 (2002) 207–222.* © 2002 Académie des sciences/Éditions scientifiques et médicales Elsevier SAS

mécanique des fluides numérique / ligne de contact mobile / champ de phase / effets de retard dus à la cinétique

1. Introduction

In his monumental work on capillarity theory, Laplace already saw what he called 'viscosity' as a source of discrepancies between observations and his and Thomas Young's theory. He states it as follows: "La viscosité des liquides, loin d'être la cause des phénomènes capillaires, en est une cause perturbatrice. Ils ne sont rigoureusement conformes à la théorie que dans des liquides qui jouissent d'une fluidité parfaite: car les forces dont ces phénomènes dépendent sont si petites que le plus léger obstacle peut en modifier les effets d'une manière sensible", which translates into: "Viscosity of liquids, far from being the cause of capillary phenomena, is a source of perturbation. Theory is followed exactly in liquids of perfect fluidity only; the relevant (i.e., capillary) forces are so small that the slightest cause may change their effects significantly", P.H. Laplace, Second supplément au livre X of *Traité de mécanique céleste*, p. 491, Archives de l'Académie des sciences, Paris. It is interesting to point out that viscosity was already understood by Laplace, years before the concept was formalized in the writing of the Navier–Stokes equations. Later he explains the discrepancies between the observations of Newton and Hauy and his own explanation of Jurin's law of the rise of liquids in capillaries to the impossibility of molecules close to the solid to move with respect to this solid (nowadays such a discrepancy is explained by contact angle hysteresis on heterogeneous solids). It seems fair to attribute to Laplace the idea that the impossibility of fluid motion near solid surfaces makes it hard for a liquid-vapor interface to reach equilibrium under capillary forces. It is perhaps at this point that a word of caution should be made: in simple fluids there is only one kind of force, the molecular interactions. It is sometimes quite confusing, if not wrong, to see viscosity (and generally non equilibrium process) as generating forces and stresses that are to be added, or balanced with equilibrium forces, supposedly of a different nature. Indeed, this is fully justified in classical fluid mechanics, where equilibrium pressure is added to viscous stress in the Navier–Stokes equations for instance. The relationship between equilibrium capillary forces and molecular interactions is not such a trivial question. We urge the interested reader to read Laplace, who made so well the connection between short range forces and capillary phenomena (Young's essay is very hard reading and understanding, as rightly pointed out by Maxwell in his review [1]).

Young and Laplace showed that a liquid/vapor interface merges with a smooth solid surface at a well defined angle at equilibrium (a similar result applies to the merging of three fluids. Surprisingly, a four phase merging can also occur robustly along a single 'quadruple' line [2]). Let us now slide the fluid with respect to the solid, by tilting a solid plate supporting a liquid droplet in a gravity field. According to the laws of (viscous) fluid mechanics, the fluid velocity is zero on the solid surface. If one assumes that the liquid/vapor interface is a material surface, it cannot move with respect to the solid near its surface, whence

a basic difficulty absent at zero contact angle [3]. The opposite case of perfect wetting at equilibrium, reviewed in [4], will not be included in this review, that is mostly limited to situations where the equilibrium contact angle is neither 0 nor π . Besides the impossibility of moving the contact line with respect to the solid by ordinary fluid motion, it has been shown [5–7] too that, when solving the fluid mechanical problem in a liquid/vapor wedge moving on a solid, the viscous stress and the viscous dissipation diverge near the triple point. This divergence persists in more complex geometries. This question of the moving contact line was reviewed early in [8,9] and later in [10,4].

One major difficulty met when trying to ‘solve’ the moving contact line problem is to find at which scale the usual continuum mechanics breaks down and should be amended to get rid of the divergence. This is very typical of the theory of capillarity: ever since Young and Laplace it has been at the crossroads of microscopic and macroscopic physics. But, as noticed implicitly by Laplace, introducing viscosity into capillary phenomena is no simple matter. An important recent advance in this respect [11] is the notion that contact line motion can be described by coupling the van der Waals interface model and the fluid mechanical (Stokes) equations. Without a sharp liquid/vapor interface, this model is free of the above mentioned divergences. Moreover, it merges smoothly at zero velocity with the Laplace–Young equilibrium theory. This makes it very convenient for studying this kind of phenomena, although the details of its working are not trivial. In particular, the merging with the ‘outer’ Scriven–Sterling solution requires some care. Within this class of coupled van der Waals–Stokes model the contact line motion becomes possible because of the evaporation and/or condensation displaces the interface without (actually, almost without – see below) fluid motion.

At first sight it would seem that such a local phenomenon (evaporation/condensation) occurring (presumably) in a microscopic neighborhood of the moving contact line can only make a small addition to the viscous damping in the bulk, and so be a negligible effect. This is not quite true: think to a droplet sliding under the effect of gravity down an inclined plane in the Stokes (= low Reynolds number) regime. The viscous dissipation, that is the free energy lost per unit time is – in order of magnitude – the integral over the volume of the droplet of $\eta(\frac{\partial u}{\partial x})^2$, u Cartesian component of the velocity field inside the droplet, $\frac{\partial u}{\partial x}$ its spatial gradient and η shear viscosity. If the droplet slides at velocity U , the power dissipated by bulk viscous friction is of order $\eta U^2 L$, L typical macroscopic length scale, the radius of the droplet for instance. This dissipation depends linearly (up to logarithms irrelevant for order of magnitude estimates) on the size of the droplet. Therefore, any phenomenon occurring locally along the moving contact line may well yield a dissipation of the same order of magnitude (as far as the size dependence is concerned: the length of the contact line is of order L too, and the corresponding dissipation should be proportional to the total length of the line) as the bulk viscous dissipation. We shall even argue that the total dissipation (and so ultimately the speed of descent of the droplet) can be completely dominated by the contribution of the neighborhood of the contact line, where evaporation/condensation takes place.

Evaporation/condensation, a non equilibrium process, makes possible the contact line motion. It requires a thermodynamic force, in the sense of Onsager (not with the usual mechanical meaning), measuring by how much the system is out of equilibrium. This force is the difference between the equilibrium and the actual value of the contact angle, whence the mobility relation:

$$U = k F_O(\theta, \theta_{eq}) \quad (1)$$

where F_O is a dimensionless function (the subscript O is for Onsager), of order 1 that depends on the equilibrium value θ_{eq} of the contact angle and of its actual value θ . Moreover U is the in-plane velocity of the contact line. The function F_O vanishes for $\theta = \theta_{eq}$. For small velocities, a linear approximation is appropriate:

$$F_O \approx (\theta_{eq} - \theta)$$

We shall not consider the situation of an heterogeneous solid with a space dependent θ_{eq} , although it is rather widespread. The linear approximation for F_O does introduce a symmetry between the two directions of motion, advancing and receding (as seen from the liquid), although we argue that receding motion, as it requires evaporation, is much slower than advancing motion. This could be accounted for by assuming that the advancing angle is far closer to its equilibrium value and even equal to it, because the corresponding mobility factor is very large.

The mobility factor k with the dimension of a velocity should be of the order of a molecular speed, as the ratio σ/η , σ the capillary constant. For most realistic cases, this speed is fairly large, in the hundreds of meters per second range. This should make quite negligible this dependence of the contact angle with respect to the velocity of the moving line in most real situations where the contact line moves by centimeters per second. This does not take into account the possible existence of a dimensionless Arrhenius factor in (1), making k very small. References [12,13], and [14] give theoretical arguments for such a small Arrhenius factor, in agreement with recent experimental findings [15]. Such an Arrhenius factor can be found in [16], but with a slightly different meaning: it concerns the kinetics of the liquid/solid interface and arises from the need for the molecules close to the solid surface to jump from a physisorbed state on one solid/liquid interface to the other solid/liquid interface. Moreover, such an Arrhenius factor was not formally associated to a small mobility, a crucial point below. These remarks suggest the following approximation: the velocity of the moving contact line is much smaller than any molecular speed, but it may have nevertheless an important effect on the dynamics of contact line, once multiplied by the inverse of the Arrhenius factor. This yields a consistent schema of approximation for the contact line motion. Because this velocity is to be multiplied by a very large inverse Arrhenius exponential, it may have nevertheless important effects on the dynamics of molecules near the moving contact line, and so determines the dynamical contact angle, the main source of dissipation being near the contact line (this holds true when the typical droplet size for instance is less or smaller than the capillary length, otherwise the contact line motion has to be found by a local approximation; see remarks at the end). This schema works if the contact angle so defined (now velocity dependent) is neither zero nor π , that is if there is neither wetting nor drying under the effect of the fluid motion (what we call dynamical wetting later). If such a phenomenon occurs, the predictions of the theory are actually not so obvious: equilibrium wetting (the phenomenon we shall concentrate on first) is followed by the spreading of liquid on the solid surface, until it is fully covered, unless some other phenomenon stops it (the finite size of molecules yields a lower bound to the film thickness, but other effects could be at work, such as long range interactions with the solid, etc.). On the other hand, in the dynamical wetting transition, the influence of the motion is important near the contact line only, so that far from this line, the liquid has no tendency to spread on the solid. Therefore this dynamical wetting transition should show a phenomenology different of the one of usual equilibrium wetting. This is discussed in Section 6 of this review. Below, one examines the equilibrium wetting in the framework of the van der Waals theory. This is motivated by the fact, shown later, that the moving contact line is described, in the limit of slow evaporation dynamics, by equations of the same form as the equilibrium van der Waals equations, with velocity dependent quantities. Before exposing the main idea of this van der Waals dynamical theory, we comment briefly upon the existing equations for the mobility of the moving contact line (the explicit form of the relation (1)).

2. Equation(s) for the mobility

The literature proposes many relations between the velocity of the contact line on the solid and the contact angle (the mobility relation) based upon various assumptions [17–21]. An earlier publication is by Washburn [22] who studied the rise of a liquid in a capillary.

This review does not examine in details those relations, since it focus on another approach. The status of the mobility relation per se is quite ambiguous: first one may think that among all possible liquids, solids, no single relation, even with a fair supply of adjustable parameters will represent all possible physical

situations. Furthermore, the physical meaning of this kind of mobility relation, taken as such, is not clear to this author: one would expect it to enter as a boundary condition for the merging of the liquid/vapor interface with the solid. At equilibrium, the Young–Laplace equilibrium angle is a boundary condition for Laplace’s equation imposing a constant mean curvature to the surface enclosing a given volume in droplet problems. The situation is quite different for the moving contact line: the divergence of the fluid mechanical problem forbids the merging of the liquid/vapor surface with a solid surface, at least if one enforces the equation of classical fluid mechanics in their usual form and boundary conditions. Sometimes, perhaps to circumvent this difficulty, the dynamical contact angle given by the mobility relation is claimed to have meaning at ‘intermediate’ distances only, neither too close nor too far from the microscopic merging of the interface with the solid. To be relevant this would require that over a presumably short range between the ‘intermediate’ distance and the molecular neighborhood of the contact line the curvature of the interface is large enough to change appreciably its slope, something that would imply very large forces of a rather unspecified nature. No precise calculation seems to have been made supporting this. We insist here on another approach to the same problem that is a priori free of the difficulties just mentioned.

This question shows up particularly well in the lubrication approximation, reviewed recently by Pismen [23,24]. He shows that no well defined dynamical contact angle can be derived from the simple balance between capillary and viscous forces in this lubrication limit. As shown below, the large relaxation time inserted into the dynamical van der Waals theory makes it possible to get rid of the fluid mechanical problem at least close to the contact line. Farther away, the local quasi equilibrium solution can be matched with the solution of the outer fluid mechanical problem.

3. Equilibrium wetting transition in the van der Waals model

A remarkable observation related to the motion of contact line is the dynamical wetting transition: beyond a certain speed, a receding liquid/vapor surface becomes locally tangent to the solid (this occurs on the receding line because the sign of the mobility constant is constrained by the stability of equilibrium). Its most conspicuous manifestation is a cusp on the receding line beyond the critical speed for dynamical wetting [25,26]. This can be explained at small mobilities, getting rid of any riddle of the fluid mechanical problem (besides to be fully justified by the underlying physics and to agree with the experimental data). Before considering this, we shall review some results about equilibrium wetting in phase field models where there are two types of wetting transition, only one being relevant for the dynamical wetting transition. That two types of transition may show up can be deduced from an analytical approach following the methods and ideas of [27–31]. One of the wetting transitions is accompanied by an increase of the thickness of the liquid layer physisorbed on the solid, that eventually diverges at the transition. In such a case, the effect of the contact line motion becomes negligible as the transition is approached, so that this type of transition cannot be driven by the contact line motion. But there is another kind of wetting transition without the diverging thickness of the liquid layer physisorbed on the solid. In this case, it just happens that the Young–Laplace value of the contact angle goes to zero at some value of the parameters in the van der Waals phase equation. Only in this case a dynamical wetting transition can be observed.

This section will be also an opportunity to introduce the equilibrium van der Waals theory. This describes the distribution of density in a fluid, including the possibility of two phases (liquid and vapor) coexisting at equilibrium. The fluid, liquid or vapor, lies in the half space $z > 0$. This van der Waals (or phase) equation has been considered over the years by many scientists. Cahn has studied it in the general framework of phase transitions [32,33]. Gouin has published rather extensively on this topic [34–38] in relation to various applications to capillary phenomena in fluids. The van der Waals phase equation can be written as:

$$K \Delta \rho + \mu - \left(f(\rho) + \rho \frac{df}{d\rho} \right) = 0 \quad (2)$$

The mass density ρ changes continuously in space, K is a positive constant, and μ is a chemical potential necessary to adjust the total number of particles. The density takes the value ρ_l on the liquid side and ρ_v in the vapor. The function $f(\rho)$ (the notations of van der Waals) represents how the internal energy depends on density and $\Delta = \partial^2/\partial x^2 + \partial^2/\partial z^2$. In (2) μ and f are energies per unit mass. The interaction between the fluid and the solid surface is represented by a mixed boundary condition on the solid, located at $z = 0$:

$$\rho + \beta \frac{d\rho}{dz} = \rho_s |_{z=0} \tag{3}$$

ρ_s and β , given constants (ρ_s has the physical dimension of a mass density but it is not the boundary value of ρ on the solid, except if $\beta = 0$). We assume coexistence between the two fluid phases at equilibrium when μ is set to zero, which gives three conditions:

$$f(\rho_l) + \rho_l \frac{df}{d\rho_l} = f(\rho_v) + \rho_v \frac{df}{d\rho_v} = 0$$

Then the chemical potential should be the same on both sides of the interface:

$$\int_{\rho_v}^{\rho_l} d\rho \left(f(\rho) + \rho \frac{df}{d\rho} \right) = 0$$

or $H(\rho_l) = H(\rho_v)$, with $H(\rho) = \rho f(\rho)$. At equilibrium, the density $\rho(q)$ changes continuously across a flat interface (q coordinate perpendicular to the liquid/vapor interface), from ρ_v at $q = -\infty$ to ρ_l at $q = +\infty$ (for instance), it is the solution of:

$$K \frac{d^2\rho}{dq^2} - \left(f(\rho) + \rho \frac{df}{d\rho} \right) = 0 \tag{4}$$

The Young–Laplace contact angle is a consequence of Noether’s theorem [27–31] and the wetting transition occurs when the so-called Antonov relation is satisfied between the three capillary constants σ_{lv} , σ_{sv} and σ_{ls} giving the interaction energy per unit area between the liquid and vapor (σ_{lv}), vapor and solid (σ_{vs}) and liquid and solid (σ_{ls}):

$$\sigma_{sl} + \sigma_{lv} - \sigma_{sv} = 0 \tag{5}$$

To find the capillary energies one notices that the van der Waals equation together with the boundary conditions on the solid make stationary the Euler–Lagrange functional:

$$\mathcal{F} = \int dx \int_0^{+\infty} dz \left(\frac{K}{2} (\nabla\rho)^2 + H(\rho) - H(\rho_v) \right) - \frac{K\beta}{2} \int dx \left(\frac{\partial\rho}{\partial z} \right)^2 \Big|_{z=0} \tag{6}$$

The last term in (6) accounts for the mixed boundary conditions (3). The integration of (4) gives [27–31] the liquid/vapor surface tension σ :

$$\sigma_{lv} = \int_{\rho_v}^{\rho_l} d\rho \sqrt{2K [H(\rho) - H(\rho_v)]} \tag{7}$$

It does not depend on the boundary contribution to \mathcal{F} , but the two other surface tensions do:

$$\sigma_{ls} = \int_{\rho_{l0}}^{\rho_l} d\rho \sqrt{2K [H(\rho) - H(\rho_v)]} - \frac{K\beta}{2} \left(\frac{\partial\rho}{\partial z} \right)^2 \Big|_{z=0} \tag{8}$$

and

$$\sigma_{vs} = \int_{\rho_v}^{\rho_{s0}} d\rho \sqrt{2K [H(\rho) - H(\rho_v)]} - \frac{K\beta}{2} \left(\frac{\partial \rho}{\partial z} \right)^2 \Big|_{z=0} \quad (9)$$

In (8) and (9), $\partial\rho/\partial z$ is computed on the solid for $z = 0$. The corresponding solution of the van der Waals equation is such that the value of ρ for $z = 0$ is ρ_{l0} ($/\rho_{v0}$), although it tends to ρ_l ($/\rho_v$) at infinity. From the integral of motion of the van der Waals equation in 1D:

$$\frac{K\beta}{2} \left(\frac{\partial \rho}{\partial z} \right)^2 \Big|_{z=0} = \beta (H(\rho_{l0}) - H(\rho_v))$$

A similar expression holds for the vapor–solid surface tension. The final expressions of σ_{ls} and σ_{vs} can be written as:

$$\sigma_{ls} = \int_{\rho_{l0}}^{\rho_l} d\rho \sqrt{2K [H(\rho) - H(\rho_v)]} - \beta (H(\rho_{l0}) - H(\rho_v)) \quad (10)$$

and

$$\sigma_{vs} = \int_{\rho_v}^{\rho_{s0}} d\rho \sqrt{2K [H(\rho) - H(\rho_v)]} - \beta (H(\rho_{s0}) - H(\rho_v)) \quad (11)$$

From the integral of motion and the boundary condition, ρ_{l0} and ρ_{s0} are roots of:

$$\frac{K}{2} \left(\frac{\rho_s - \rho_{i0}}{\beta} \right)^2 = H(\rho_{i0}) - H(\rho_v) \quad (12)$$

where the label i is for l or v . We shall now use the simplest possible function $H(\rho)$ to look at the wetting transition as a function of the parameters β and ρ_s . This is not directly relevant for the problem at hand: there the boundary conditions are constant and the potential $H(\rho)$ changes as a function of the velocity of the contact line. Nevertheless, the discussion is far easier in the present framework and show the existence of two different wetting transitions. Thanks to the constant of integration of the 1D van der Waals equation, there is no need to actually solve it. One needs only to perform the integrals over ρ that give the surface tensions and to put at the end the values of ρ_{0l} and ρ_{0v} from (12). Following [27–31] one chooses for $H(\rho)$:

$$H(\rho) = +\frac{1}{8}\rho^2(2 - \rho)^2$$

The density of the two bulk phases are $\rho_v = 0$ and $\rho_l = 2$. They are dimensionless, although physical dimensions could be restored. The values of ρ_{0l} and ρ_{0v} are found concretely by solving (12), that becomes:

$$\lambda(\rho_s - \rho) = \pm \frac{1}{2}\rho(2 - \rho) \quad (13)$$

where $\lambda = \sqrt{K}/|\beta|$ is dimensionless. The two Eqs. (13) yields four roots at most, out of which two should be selected, ρ_{0l} and ρ_{0v} . The discussion becomes a bit involved from now on, depending on the sign of β , and on the value of ρ_s . For the purpose of showing our point, it is enough to find values of ρ_s and λ such that (5) is satisfied. A simple example of it is with $\rho_s = 0$. In this case, the vapor solid layer is just a layer of constant $\rho = 0$, so that $\sigma_{sv} = 0$. From (13), $\rho_{0l} = 2(\lambda + 1)$. From the boundary condition the derivative $d\rho/dz$ is negative, as it should, if $\rho_{0l} = 2(\lambda + 1)$ at $z = 0$. The Antonov condition becomes

$$\sigma_{sl} + \sigma_{lv} = 0$$

In the present model $\sigma_{lv} = \frac{2\sqrt{K}}{3}$ and $\sigma_{vs} = \frac{\sqrt{K}}{6}(4 - (1 + \lambda)^2(2 + 11\lambda))$. From the Antonov relation, one deduces that λ is the real root of $(1 + \lambda)^2(2 + 11\lambda) = 8$, that is $\lambda = 0.2694690\dots$ This van der Waals model presents a wetting transition without infinite thickening of the liquid layer physisorbed on the solid.

The other wetting transition would correspond to the solution $\rho_s = 2 = \rho_{0v}$ of (13), that is to an infinitely thick layer of liquid in between the solid and the vapor. This cannot be the case at a dynamical wetting transition.

4. Dynamical phase field equations

In the van der Waals theory, a wetting transition may occur without divergence of the thickness of the liquid layer on the solid. A transition with divergent thickness would make the stresses due to fluid motion vanish across the interface, so that dynamical effects would become less and less important close to the transition. This excludes any dynamical transition due to the motion of the contact line if associated to a diverging thickness of the physisorbed layer.

Below, we outline the principles of contact line dynamics in phase field models. There, a dynamical wetting transition is possible at speeds far below those making the capillary number of order 1 (or velocities of order of large molecular velocities). This phenomenon of dynamical wetting, known for some time [25], was explained by assuming a functional dependence of the contact angle with respect to the velocity, and then setting the angle to zero to get the limit velocity, which does not yield much information on the microscopic process at work.

The coupled fluid and phase equations have been studied recently in [11], and [27–31], with an expression for the stress borrowed from [39]. The time independent (see below for the meaning) continuity equation takes the form:

$$\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho w)}{\partial z} = 0 \tag{14}$$

with $u(x, z)$ fluid velocity in the x direction (parallel to the solid) and w in the z direction (normal to the solid). ρ is kept inside the divergence operator, because it can change continuously across the liquid/vapor interface.

The momentum balance in the x direction becomes:

$$\frac{\partial(T_{(xx)} + S_{(xx)})}{\partial x} + \frac{\partial(T_{(xz)} + S_{(xz)})}{\partial z} = 0 \tag{15}$$

The Cartesian components of T are:

$$T_{(xx)} = \rho f(\rho) + \frac{K}{2}(\rho_z^2 - \rho_x^2) \tag{16}$$

and

$$T_{(xz)} = -K\rho_x\rho_z \tag{17}$$

The notations in (16) and (17) are ρ_x for $\partial\rho/\partial x$, etc. The components of tensors like T are denoted as $T_{(xx)}$, $T_{(xz)}$, etc. The components of the viscous stress are:

$$S_{(xx)} = 2\eta\frac{\partial u}{\partial x} + \left(\zeta + \frac{2}{3}\eta\right)\text{div}(\mathbf{u}) \tag{18}$$

and

$$S_{(xz)} = \eta\left(\frac{\partial u}{\partial z} + \frac{\partial w}{\partial x}\right) \tag{19}$$

Similar equations apply in the z direction. In Eqs. (18), (19) ζ is for the volume viscosity and $\text{div}(\mathbf{u}) = \frac{\partial u}{\partial x} + \frac{\partial w}{\partial z}$.

The equilibrium stress tensor $T_{(.,.)}$ is derived from the Euler–Lagrange functional (Eq. (6)) through the Noether invariant associated to translations in the x and z directions:

$$T_{(xx)} = -\rho_x \frac{\delta \mathcal{F}}{\delta \rho_x} + \mathcal{F}$$

$$T_{(xz)} = -\rho_x \frac{\delta \mathcal{F}}{\delta \rho_z}$$

$$T_{(zz)} = -\rho_z \frac{\delta \mathcal{F}}{\delta \rho_z} + \mathcal{F}$$

Without fluid motion, the condition for the stress balance becomes:

$$\frac{\partial T_{(xx)}}{\partial x} + \frac{\partial T_{(xz)}}{\partial z} = 0$$

This follows from the equilibrium van der Waals equation (2).

Eqs. (18) and (19) being intended to apply to both the vapor and the liquid, η and ζ are expected to vary significantly from one phase to the other. The set (2), (14) and (15) is consistent (= same number of unknowns and of equations) because of the free ‘gauge’ μ , a function of x and z now, makes compatible the phase and continuity equations, both imposed to ρ . In a frame of reference moving at constant speed U with respect to the solid in the x direction all quantities like ρ , u , etc. become independent on time and the velocity U is the boundary value of u at $z = 0$, although $w|_{z=0} = 0$. It has been suggested [40] that the moving contact line problem can be solved by changing the no slip boundary condition for fluid motion (fluid velocity on the solid = velocity of the solid wall itself). Close to the solid, one expects some sliding. But it is not clear altogether that this is enough to get rid of the difficulties: if one maintains that the interface is a material surface down to the contact line, it has to get very large curvature to stand the normal pressure difference across it, that is unbalanced in the Hu–Scriven solution. Moreover, once some slip is permitted, there remains to determine the dynamical contact angle. The approach developed below does everything in a single sweep and does not require to change the boundary condition for the fluid motion, although this could be included in principle.

The set of Eqs. (2), (14) and (15) has been the subject of recent studies [11] but without the kinetic retardation effects, although they are crucial to represent the observations. Moreover they lead to some interesting analysis, both from the point of view of the microscopic theory and for the macroscopic equations themselves.

We noticed already (Eq. (6)) that the phase Eq. (2) makes stationary an Euler–Lagrange functional, a condition like $\delta \mathcal{F} / \delta \rho = 0$, where $\delta(\cdot) / \delta \rho$ is the usual functional derivative and where:

$$\mathcal{F} = \int dx dz \left(\frac{K}{2} |\nabla \rho|^2 + H(\rho) - \mu \rho \right) \quad (20)$$

Boundary terms in the Euler–Lagrange functional (6) have been discarded in (20), because of the qualitative character of the discussion to follow. The Euler–Lagrange functional reaches an extremum if the system has enough ‘time’ to reach this state. Therefore, a direct way of introducing slow Arrhenius kinetics into this theory is to assume that the relaxation to equilibrium, as represented by the phase equation, is not instantaneous, but takes some time. We replace the ‘quasiequilibrium’ phase equation $\delta \mathcal{F} / \delta \rho = 0$ by the dynamical equation

$$\tau \frac{\partial \rho}{\partial t} = - \frac{\delta \mathcal{F}}{\delta \rho}$$

with τ proportional to the long relaxation time, that is to the inverse of a very small Arrhenius exponential.

A large constant τ assumes that it takes a long time everywhere to reach equilibrium, although our argument for the small Arrhenius factor (and for a long time scale) concerns the dynamics of change from liquid to vapor only. This would point to a time scale depending, among other things, on the density, and being large in the transition layer only. To take this into account would enormously complicate the analysis without altering it fundamentally. As the equation needs to be Galilean invariant, the left hand side of the dynamical phase equation should be

$$\tau \left(\frac{\partial \rho}{\partial t} + u \frac{\partial \rho}{\partial x} + w \frac{\partial \rho}{\partial z} \right)$$

The modified van der Waals equation is derived from this dynamical equation by assuming steadiness in the moving frame of reference:

$$\tau \left(u \frac{\partial \rho}{\partial x} + w \frac{\partial \rho}{\partial z} \right) = K \Delta \rho + \mu - \left(f(\rho) + \rho \frac{df}{d\rho} \right) \quad (21)$$

Now we have set the stage (= written Eqs. (14), (15) and (21)) and can proceed to solve them in the appropriate limit.

5. Flow structure in the transition layers

This section outlines the solution of the coupled equations in the large activation energy limit, and in the neighborhood of the triple contact. A rather remarkable property of the coupled equations is that the contact line motion yields a change of the parameters of the van der Waals equilibrium equation, making it possible to have a velocity-driven wetting transition very similar to the one found at equilibrium. This local solution can be matched with the large scale flow [12,13].

Because there is no sharp liquid/vapor interface in this theory, divergences and discontinuities of the solution of the Stokes problem in a wedge disappear. Nevertheless, it becomes difficult then, if not impossible, to continue an analytic approach, except in the lubrication limit [27–31].

When (21) holds, one may rewrite the contribution of internal stresses to the momentum balance as:

$$\frac{\partial T_{(xx)}}{\partial x} + \frac{\partial T_{(xz)}}{\partial z} = +\tau \rho_x \operatorname{div} \mathbf{u} - \rho \frac{\partial \mu}{\partial x}$$

and a similar expression for the z component. In the limit where U is much smaller than σ/η , τ can be big enough to bring the product $U\tau$ to be of the same order of magnitude as the other terms in the phase equation. In this limit the viscous stress S becomes negligible compared to $T_{(ij)}$. This does not hold uniformly; it is true only wherever the density is changing on scales of order $K^{-1/2}$, that is near the solid surface and in the transition layer between liquid and vapor. Far from those layers, the viscous stress is of the same order as the internal stress, and $T_{(ij)}$ becomes the usual pressure needed to adjust the incompressibility condition [12,13].

Wherever the contribution of the viscous stress to the momentum balance is negligible, one can reduce the integration to the problem of finding two functions of one variable, $F(\rho)$ and $G(\rho)$.

This flow structure can be computed rather explicitly thanks to the hyperbolic structure of the relevant equations. Without viscous stress, the momentum balance becomes:

$$-\tau \frac{\partial \rho}{\partial x} (u \rho_x + w \rho_z) - \rho \mu_x = 0 \quad (22)$$

and

$$-\tau \frac{\partial \rho}{\partial z} (u \rho_x + w \rho_z) - \rho \mu_z = 0 \quad (23)$$

Using mass conservation, this gives:

$$\tau \frac{\partial \rho}{\partial x} \operatorname{div} \mathbf{u} - \mu_x = 0 \quad (24)$$

and

$$\tau \frac{\partial \rho}{\partial z} \operatorname{div} \mathbf{u} - \mu_z = 0 \quad (25)$$

where $\operatorname{div} \mathbf{u} = u_x + w_z$.

The set (24) and (25) can be solved formally. Taking the curl one obtains:

$$\rho_x (\operatorname{div} \mathbf{u})_z - \rho_z (\operatorname{div} \mathbf{u})_x = 0$$

which shows that $\operatorname{div} \mathbf{u}$ is a function of ρ only, say $\operatorname{div} \mathbf{u} = F(\rho)$. Putting this into (24) or (25), one obtains

$$\mu = \tau \int^\rho d\rho' F(\rho') \quad (26)$$

Using those results in the dynamical phase equation, one gets:

$$K \Delta \rho - \left(g(\rho) + \rho \frac{dg}{d\rho} \right) = 0 \quad (27)$$

where $g(\rho) = f(\rho) - \tau \int^\rho d\rho' F(\rho')$. It is quite remarkable that the problem of finding the density distribution near the triple point has been transformed into a problem of the same form as the equilibrium van der Waals equation, but with a new $g(\rho)$ replacing the original $f(\rho)$ (the boundary condition for ρ at $z = 0$ being the same as before). The way $F(\rho)$ and the constant of integration in (26) are found is explained now.

The relationship between $F(\rho)$ and the velocity field follows from the definition:

$$u_x + w_z = F(\rho)$$

Let us introduce the stream function $\Psi(x, z)$ such that $\rho u = -\frac{\partial \Psi}{\partial z}$ and $\rho w = \frac{\partial \Psi}{\partial x}$. It is related to F by:

$$\rho_z \Psi_x - \rho_x \Psi_z = -\rho^2 F(\rho) \quad (28)$$

Using now as coordinates ρ and the curvilinear distance along the isodensity lines, say s , (28) becomes:

$$\frac{\partial \Psi}{\partial s} = \frac{\rho^2 F(\rho)}{|\nabla \rho|} \quad (29)$$

where $|\nabla \rho| = \sqrt{\rho_x^2 + \rho_z^2}$ is a priori a function of ρ and s . The solution of (29) takes the following form:

$$\Psi(\rho, s) = G(\rho) + \rho^2 F(\rho) \int_0^s \frac{ds}{|\nabla \rho|} \quad (30)$$

The integration constant, $G(\rho)$, a function of ρ , is yet to be found. We shall take $s = 0$ as equivalent to $z = 0$, which assumes that the isodensity line crosses the $z = 0$ plane (see below).

The boundary conditions to be imposed on this solution will become ultimately a set of conditions defining F and G . One boundary condition comes from the imposed flow velocity on the solid surface. Since Eq. (29) is first order, it matters to know if the isodensity line on which Ψ is computed crosses or not the solid at $z = 0$. The mixed boundary conditions (3) imply that the solid surface is crossed by isodensity lines in a finite density interval $[\rho_a, \rho_b]$. The density ρ_a is the value of ρ at $z = 0$ such that a one dimensional solution of the phase equation (Eq. (4) with g replacing f and the boundary condition (3)) reaches ρ_v at infinite z . Similarly ρ_b is the value of ρ on the solid when ρ tends to ρ_l at infinity. Those two situations, ρ tending to either ρ_v or ρ_l as z tends to infinity are realized far from the contact line, that is for x tending to plus or minus infinity. Therefore one expects that for any finite x and $z = 0$ the value of ρ on the solid is in between the extreme values ρ_a and ρ_b (as a function of x $\rho(x, z = 0)$ might happen not to be increasing or decreasing monotonously in between its limit values at plus and minus infinity, so that it could take values outside of the interval $[\rho_a, \rho_b]$; we assume this does not happen). In this range of values of ρ , the function $\Psi(s, \rho)$ should satisfy two boundary conditions for $s = 0$, one asserting that $u = -\Psi_z/\rho$ is equal to U , the imposed translation speed of the solid. The other condition states that the velocity normal to the solid, w , vanishes at $z = 0$. Indeed these two conditions are somewhat implicit, since they are imposed to Ψ , that depends itself on F , which ultimately enters into the phase equation that gives the density distribution near the solid. Nevertheless, the number of unknown functions is equal to the number of conditions: they are two conditions for Ψ at $z = 0$, and there are two unknown functions as well, $F(\rho)$ and the constant of integration $G(\rho)$.

From (30):

$$F(\rho) = U \left. \frac{\partial \rho}{\partial x} \right|_{z=0} \tag{31}$$

and

$$\frac{dG}{d\rho} = U \left. \frac{\rho \rho_z}{\rho_x^2 + \rho_z^2} \right|_{z=0} \tag{32}$$

The function $\rho(x, z)$ that enters into (31) and (32) is itself the solution of the modified van der Waals equation (27) subject to the boundary condition (3). The right-hand sides of (31) and (32) become functions of ρ , as do the left sides, once $\rho(x, z = 0)$ is known.

It remains to settle the case of the isodensity lines not reaching the solid: along those lines ρ lies either in $[\rho_v, \rho_a]$ or $[\rho_b, \rho_l]$. At $|x|$ infinity, they tend to horizontal straight lines at constant non zero z . One expects that the liquid/solid and vapor/solid transition layers are unaffected by the fluid motion there, since the flow lines are parallel to the isodensity lines, which cancels any interaction between the fluid flow and the density gradient. Therefore, the transition layers (solid/vapor and liquid/vapor) should tend to their 1D equilibrium shape. One should have $F(\rho)$ equal to zero in $[\rho_v, \rho_a]$ and $[\rho_b, \rho_l]$. This is consistent with the limit value of F at x tending to infinity as it results from (31): there $\rho(x, z)$ becomes a function of z only so that F tends to zero. Similarly, near the surface of the solid one expects the velocity to become uniform, horizontal and equal to U . This is consistent with the limiting form of the equation (32) when $\rho(x, z)$ depends on z only. In this limit case, it integrates to

$$G = U \int_0^z dz' \rho(z') \tag{33}$$

where an irrelevant integration constant has been set to zero. This shows why it is important to have mixed or Neuman boundary condition for the phase equation at $z = 0$: with a pure Dirichlet condition the present method of solution fails because it gives a non continuous function F , and a non smooth stream function Ψ as well. Since the viscous stress S depends on higher derivatives of Ψ than the stress T , the assumption

that S is dominated by T in the transition layer cannot be kept anymore for a non smooth Ψ . Therefore, for the Dirichlet boundary condition, another approximation schema would be necessary, different from the one presented here that rests on that S is much smaller than T in the transition layer. The Neuman condition $\frac{\partial \rho}{\partial z} = 0$ at $z = 0$ would give $G = 0$ and $F(\rho) = U \frac{\partial \rho}{\partial x}$ at $z = 0$. This would yield sensible results and make a special case of the general mixed boundary conditions. The mixed boundary conditions with more parameters have more flexibility than Neuman's condition to represent real physical situations.

It remains to find the integration constant in μ , given formally by $\mu(\rho) = \tau \int^{\rho} d\rho' F(\rho')$. Once the function $F(\rho)$ is known, the only unspecified constant is this integration constant. The function $g(\rho) = f(\rho) - \tau \mu(\rho)$ should satisfy three conditions, namely that $\frac{d(\rho g)}{d\rho} |_{\rho=\rho_l} = \frac{d(\rho g)}{d\rho} |_{\rho=\rho_v} = 0$, which defines ρ_l and ρ_v for any arbitrary constant of integration added to μ (provided that $g(\rho)$ has the right shape, something we shall assume). The third condition is the Maxwell condition: $\rho_l g(\rho_l) = \rho_v g(\rho_v)$. It is a single equation for one parameter, the constant of integration in μ , which is specified in this way. Let us notice that the 'equilibrium values' of the vapor and liquid density so defined are in general different from their values in the bulk phases at the true equilibrium (at equilibrium f replaces g in van der Waals equation).

In the small U limit (actually small $U\tau$ limit) Eqs. (31) and (32) give F and G in a very simple way, once the equilibrium density distribution near the triple contact line is known. At the lowest order (in U) it is enough to put the equilibrium distribution $\rho(x, z)$ into (31) and (32).

The present model is consistent with the existence of a dynamical wetting transition. At equilibrium, the function $f(\rho)$ together with the mixed boundary condition may be such that the contact angle is not zero. The motion changes this function by a finite amount into the function $g(\rho)$, which can be associated to a zero contact angle. The same can be said of a dewetting transition.

6. Moving contact line at the macroscopic scale: theory and experiments

The previous Section intended to show that a divergence free theory of the moving contact line can be developed by extending to non equilibrium situations the van der Waals phase field model. The final result is a kind of mobility relation between the contact angle and the speed of displacement of the triple line (this relation would follow from the application of the Young–Laplace condition for the contact angle derived from the parameters of the dynamically modified van der Waals theory). The difference between this mobility relation and others in the literature is more in its meaning than in its form: the present mobility relation is a kind of constitutive relation, and the deviation out of the equilibrium value becomes significant, as observed, at speeds far less than the microscopic speed (namely for very small capillary numbers). By taking advantage of the small capillary number limit, a well defined computational scheme for flows with a moving contact line can be devised.

In this limit, the viscous stress is negligible compared to capillary stresses (unless, of course the capillary stress is zero, see remarks below). Therefore the shape of the surface can be computed by solving Laplace's equation (constant mean curvature of the interface) with eventually other forces, like gravity, added to capillarity. The boundary condition, contrary to the familiar equilibrium case is not a fixed contact angle anymore, but it is the shape of the contact line. This yields a well defined (and non constant in general) value for the contact angle, that can be used for computing the velocity of the contact line, via the mobility relation between the contact angle and the velocity of the line. By taking a velocity linear in the difference between the actual value of the contact angle and its equilibrium value, dynamical problems have been solved [41], such as the one of a flat droplet sliding down an inclined plane. The solution shows an interesting feature: beyond a certain speed (depending for instance on the angle of the plane with respect to the horizontal), the mathematical solution becomes unphysical because the liquid/vapor mathematical surface crosses the solid. This happens on the receding part of the contact line and the mobility relation predicts a zero contact angle at the dynamical wetting transition. Beyond the critical speed, the physical solution can be analysed in the same way, but by leaving the possibility of a cusp along the contact line to get rid of unphysical solutions. Such cusps have been observed [25,26]: in particular the dependence of the cusp angle near onset

is in good agreement with this simple theory. The cusp angle [25] is such that along its sides the velocity is the critical speed in the direction normal to the contact line (a relation reminiscent of the Mach relation for shock waves). Let φ be the angle between the direction of motion and the normal to the local orientation of the contact line, so that $\varphi = 0$ if the smooth contact line slides perpendicular to the direction of motion. Beyond the critical speed $U = U_c/\cos(\varphi)$, where U_c , the critical speed, is such that $U_c = kF_O$ ($\theta = 0, \theta_{eq}$) in the mobility equation (1). Moreover, the (observed) shape of the surface near the cusp is a hyperbolic saddle, as predicted by the theory.

Another interesting possibility is the dynamical dewetting transition. Consider a solid plate dipped in a fluid and perfectly wet by it: at zero speed the contact angle is zero and the fluid climbs along the plate to form a meniscus in a gravity field as is well known (this would happen for instance with water and many solids, with liquid Helium and most solids, etc.). Let the plate be dipped into the liquid at constant speed (with a rotating drum): the triple merging depends dynamically on the speed (indeed this effect would be enhanced by a mobility law with a small Arrhenius factor, which would be present for a non volatile fluid for which the molecules of fluid would have to move from one physisorbed layer to another as the contact line sweeps the solid). If the wetting occurs without divergence of the thickness of the physisorbed liquid layer, the interactions of the fluid with the solid may be such that beyond a certain speed, the velocity dependent van der Waals potential induces a transition to a finite contact angle: beyond this critical speed the contact angle becomes finite. This would be a dynamical dewetting transition. No cusp is to be expected there since no Mach like relation on the sides of the cusp can be satisfied.

An interesting observation, by Beysens and collaborators [15] is the very long merging time of two drops on a horizontal solid: if the mobility were of order 1 in molecular scales, one would expect the merging to occur at capillary numbers of order 1. The merging was observed to be approximately 10^7 times slower than the simple prediction derived from the balance between capillary and viscous forces! This spectacular phenomenon was interpreted with the theory with a small Arrhenius factor, a theory devised before the observations were first reported.

This mobility relation and the neglect of the viscous forces cannot be universally true: if one thinks of the upstream (or downstream) edge of a large layer of liquid flowing down an inclined slope, the speed of descent will result from the balance between gravity and viscosity inside the layer. This will determine the speed of the front edge. Therefore, if this speed is much less than molecular speeds, as is often the case, one can still neglect the viscous forces to find the shape of the front bulge and use the mobility relation to determine the angle of merging along the contact line.

Curiously, although it has been known for some time, as far as I am aware of, no attempt has been made to study systematically the dynamical wetting transition. A way to observe it could be to draw a wire out of a liquid: if the wire diameter is much smaller than the capillary length, the meniscus should remain axisymmetric. The wetting transition should be between a Landau–Levich liquid film carried along the wire at large drawing speed and a meniscus at finite contact angle at low speed.

7. Summary and conclusion

The moving contact line problem can be reduced to coupled phase field equations, equations for momentum balance and mass conservation. An interesting and physically relevant limit is the one of a large transit time across the interface and of a small velocity of the contact line, the product of the large time scale and of the small velocity being of order one in molecular units. The corresponding analysis rests on a non uniform approximation, with different regions involved. The core is the molecular neighborhood of the moving contact line where the equations, if not solved, can be nevertheless analyzed rather completely. Far from the moving contact line, there is a kind of jet close to the liquid/vapor interface and the inner structure of the interface relaxes toward its equilibrium state over a (large) distance of order $\tau^{1/2}$: in physical terms this length scale would be approximately a molecular length times the inverse of the square root of the (small) Arrhenius factor perhaps within range of observability. The close neighborhood of the moving

contact line is fully dominated by the balance of forces related to the evaporation/condensation phenomena. Those forces are needed to accelerate or slow down the fluid as its velocity changes. Farther away from the moving contact line, the things are still different from the predictions of the sharp interface modelisation, because the boundary condition along the transition layer are different of the usual continuity relations of normal and tangential stress. This continues until distances of the moving contact line of order $\tau^{1/2}$. Farther away, this solution merges with the Hu–Scriven solution, the balance of normal stress being insured by a small evaporation or condensation rate. At a macroscopic scale, this theory yields various predictions agreeing well with the observations. Perhaps one can claim at this step that, if the problem of the moving contact line is not completely solved, there is good chance that this will be in the near future!

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