

## DYNAMICS OF A VISCOUS LIQUID WETTING A SOLID VIA VAN DER WAALS FORCES\*

O. V. Voinov

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Transient flows of thin films wetting a solid surface via van der Waals forces are examined. Boundary conditions are formulated on the moving wetting line and on the boundary with a very thick film which give a closed description of the dynamics of ultrathin films spreading from drops. Approximate time-dependent solutions of the boundary problem are obtained for short times. A strong limitation is found on the quasi-stationary theory of precursor films spreading from drops, and the importance of considering the inherent transience of the flow is demonstrated. A transient "truncation" of the quasi-stationary precursor film was established which gradually absorbs the whole film. A region was found where the boundary condition can be applied on the boundary with a very thick film (a "piston"). The condition on the moving wetting line is suitable for any transient problems if the liquid wets the surface well enough. It is shown possible to use a boundary layer considering capillary forces on the wetting line for the transient equation of an ultrathin film.

Asymptotic time-dependent solutions were found for the nonlinear boundary problem. Solutions were found for the movement of the wetting line in the case of a fixed piston and a semi-infinite film, and their similarities were established. Self-similar solutions were found for plane and axially symmetric pistons, and the limiting spreading was found at large distances. Non-self-similar spreading was solved for slow piston movement. An asymptotic formula was found that describes axially symmetric spreading of drops. The effect of the unusually slow approach to the limiting dependencies was obtained. The boundary problem was solved considering the delayed van der Waals interaction, which substantially changes the form of the time-dependent equation. The most general point is that the asymptotic velocity of the wetting line is  $v_* = \text{const}/\sqrt{t}$  in all the solutions, which gives them a universal meaning.

### § 1. TRANSIENT MODEL OF AN ULTRATHIN VISCOUS LIQUID FILM WETTING A SOLID

**1.1. Formulating Dynamic Problems of Thin Wetting Films.** Transient flows of a thin viscous liquid film over a flat solid surface can be described in the wetting-theory approximation with a constant pressure  $p$  over the film cross section. If the film thickness  $h(x,t)$  is small enough, where  $x$  is the two-dimensional radius vector on the solid surface and  $t$  is time, pressure contributions can come from the van der Waals long-range molecular forces

$$p = p_0 - \sigma \Delta h + A / (6\pi h^3), \quad A = A_{11} - A_{12},$$

as well as the capillary pressure (the Laplacian component of  $p$ ). Here  $p_0$  is the pressure above the free surface of the film;  $\sigma$  is the surface tension coefficient; and  $A_{11}$  and  $A_{12}$  are the Hamaker constants, which characterize the interaction of unit volumes of liquid (subscript 1) and the solid (subscript 2) (see [1] and [2], for example). For the case of wetting films,  $A < 0$  (hereafter we set  $A = -A'$ ). The dependence of  $p$  on  $h$  can go as  $h^{-4}$  instead of  $h^{-3}$  if the interaction is significantly retarded.

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We require that the scale  $L$  over which the film thickness changes be much larger than the scale  $l$  over which the capillary forces act, and that the contribution of the van der Waals forces have the same order of magnitude:

$$L \gg l = h^2(2\pi\sigma/A')^{1/2}. \quad (1.1)$$

Then the movement of the film is described by the equation

$$\frac{\partial h}{\partial t} + \text{div}(hv) = 0, \quad v = -\frac{A'}{6\pi\mu h^2}\nabla h, \quad (1.2)$$

where  $\mu$  is the dynamic viscosity and  $v$  is the liquid velocity, or

$$\frac{\partial h}{\partial t} = \kappa\Delta \ln h, \quad \kappa = A'/6\pi\mu. \quad (1.3)$$

Boundary problems for Eq. (1.3) are of interest in connection with the spreading of drops and films over a solid surface. There are quasi-stationary film flow models [3-5], and a problem for (1.3) with rapid transients was studied on an infinite line [6] without specifying boundary conditions. The formulation of boundary problems requires primarily the condition on the wetting line  $\mathbf{x} = \mathbf{x}_*(t, \varphi)$ , which divides the dry and wet part of the solid surface ( $\varphi$  is a parameter, and the subscript \* indicates values on the wetting line). We assume that the film thickness is some small constant  $h_*$  on the wetting line. Because there are no mass sources or sinks on the wetting line, its velocity coincides with the average liquid velocity  $v$ . Then conditions on the wetting line are written as follows:

$$h(\mathbf{x}_*, t) = h_*, \quad \frac{\partial \mathbf{x}_*}{\partial t} = \mathbf{v}(\mathbf{x}_*, t). \quad (1.4)$$

Obviously,  $h_*$  must exceed several molecular dimensions, so that the continuous-medium approach makes sense. If  $h_*$  is large enough, the first condition (1.4) can lead to a "truncation" of the stationary film flow [5] obtained from the stationary equations by considering capillary pressure. We note that if the macroscopic (equilibrium) film thickness has a minimum, then the boundary condition (1.4) for Eq. (1.3) can be obtained analytically (see section 1.5).

For stationary film flow, when the film profile  $h(x)$  translates with a constant velocity, its shape does not depend on the conditions (1.4). However, the main problems of interest are those in which the shape of the film is closely related to conditions on the wetting line (1.4). This requires examining highly transient problems.

**1.2. Formulating Problems of Films Spreading from Drops.** A thin film which moves via van der Waals forces can border with a very thick film. Such films are called primary films [7] or precursor films [5], or even more simply p-films. A p-film can transform into a much thicker film, which, under the influence of capillary forces, forms a dynamic contact angle with the solid surface [4, 5].

In order to evaluate the sharp transition from a p-film to a thicker film, we must know the singularities of the p-film thickness on its boundary. In the one-dimensional case

$$h \rightarrow \infty, \quad x \rightarrow x_0(t). \quad (2.1)$$

We note that the stationary solution [3, 4] of the form  $h(x - vt)$  also has a singular point. A quasi-stationary description of the dominant term as  $x \rightarrow x_0$  can be written on the basis of the simple solution  $h \sim (x - x_0)^{-1}$ . This yields a continuity condition on the liquid velocity at the point  $x = x_0$ :

$$v = -\frac{\kappa}{h^2} \frac{\partial h}{\partial x} \rightarrow \frac{dx_0}{dt}, \quad x \rightarrow x_0. \quad (2.2)$$

This condition allows the singularity in the moving point  $x_0(t)$  to be represented as a particular piston pushing on the edge of the p-film.

The initial conditions at  $t = 0$  can be most simply specified by assuming that there is no p-film at  $t = 0$  and that the film forms at  $t > 0$ . Then we must specify the wetting line at  $t = 0$  which coincides with the piston:

$$x_* \rightarrow x_0, \quad t \rightarrow 0. \quad (2.3)$$

In spreading-drop problems, we are interested in the power-law dependence of the piston coordinates as a function of time:

$$x_0 = at'. \quad (2.4)$$

Here the transformation

$$\begin{aligned} h &= h'h_*, x = x'X, t = t'T, X = a^n(h_*/\varkappa)^n, \\ T &= a^{2n}(h_*/\varkappa)^n, n = 1/(1 - 2\varepsilon) \end{aligned} \quad (2.5)$$

reduces Eq. (1.3) and the boundary conditions to

$$\varkappa = a = h_* = 1, \quad (2.6)$$

when the transient boundary problem for (1.3) contains a single parameter  $\varepsilon$ . Obviously the case (2.6) is general without restrictions; therefore we will omit the primes on  $h$ ,  $x$ , and  $t$  for brevity.

The inner region  $x < x_0$  is described using the asymptotic model ( $\mu\nu/\sigma \rightarrow 0$ ) of a spherical segment and the formula for the slope angle of a free boundary [4, 8]:

$$\alpha = [(9\mu\nu/\sigma)\ln(h/h_m)]^{1/3}.$$

If the drop spreads axisymmetrically (see Fig. 1), the dynamic angle  $\alpha_0 \sim t^{-3/10}$  [8]; therefore  $\varepsilon = 1/10$  in (2.4). In the plane case,  $\varepsilon = 1/7$ .

In (2.4),  $a$  is approximately constant, and can be written as [8]

$$a = R(\sigma/R\mu c_0)^{1/3}, c_0 = c_1 \ln(h_0/h_{\max}), \quad (2.7)$$

where  $R$  is the radius of a sphere (or circle) with an equivalent volume  $V$  (or area  $S$ );  $c_1 \approx 0.0125$  in the plane case, and  $c_1 \approx 0.006$  in the axisymmetric case;  $c_0 \approx \text{const}$  if  $h_0/h_{\max} \gg 1$ ;  $h_0$  is the same order as the thickness in the center of the central segment of the sphere (circle); and  $h_{\max}$  is the maximum thickness (to an order of magnitude) of the p-film in the transition region to the thick film [4]:

$$h_{\max} = \left(\frac{\sigma}{3\mu\nu}\right)^{1/3} \sqrt{\frac{A'}{2\pi\sigma}}. \quad (2.8)$$

From (2.7) the time and length scales in (2.6) have the form

$$\begin{aligned} T &= \frac{R\mu}{\sigma} \left(\frac{3\Omega}{c_0^2}\right)^n, X = R \left(\frac{3\Omega}{c_0}\right)^{n'}, \\ \Omega &= \frac{h_* R}{\lambda^2}, \lambda^2 = \frac{A'}{2\pi\sigma}, n = \frac{1}{1 - 2\varepsilon}. \end{aligned} \quad (2.9)$$

The dimensionless maximum thickness (2.8) in the case of a drop is

$$h'_{\max} = 2.7(\lambda/h_*)(\Omega^n t)^{(1-\varepsilon)/3}. \quad (2.10)$$

Because  $h_{\max}$  increases with increasing  $t$  it is possible to fulfill (2.2) in some range of the parameters. This requires, in particular, that the right side of (2.10) be large compared to unity.

Thus, we must solve the transient boundary problem (1.3), (1.4), (2.1)-(2.6) on the movable segment ( $x_0, x_*$ ) with an unknown boundary  $x_*$ .

We note that the Lagrange coordinate method in Stefan's problem [9, 10] can be useful in investigating this problem.

We now examine the properties of the solutions based on the movement of the p-film and illustrate the limits of its applicability.

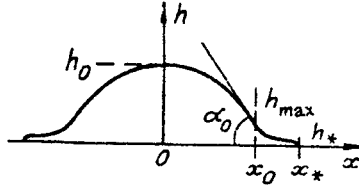


Fig. 1

**1.3. Dynamics of the P-Film near the Piston.** At small distances from the singular point  $x_0$ , it is convenient to seek the solution of (1.3) in a moving system bound to the piston:

$$\frac{\partial h}{\partial t} - v_0 \frac{\partial h}{\partial x} = \frac{\partial^2}{\partial x^2} \ln h, \quad \bar{x} = x - x_0(t).$$

By neglecting  $\partial h/\partial t$ , we have a stationary profile [3, 4] as the first approximation

$$h_{(0)} = 1/v_0 \bar{x}, \quad v_0 = x_0. \quad (3.1)$$

The length of the p-film in the quasi-stationary approximation is determined by the equation  $h = 1$ :

$$\bar{x}_* = 1/v_0 = t^{1-\epsilon}/\epsilon. \quad (3.2)$$

To the accuracy of its components, this formula corresponds to the stationary theory [5].

The condition that term  $\partial h_{(0)}/\partial t$  be small in the time-dependent equation defines region of applicability of the quasi-stationary solution (3.1)

$$\bar{x} \ll v_0^2 / |dv_0/dt|,$$

which is true in a small region near the piston.

For the function  $x_0 = t^\epsilon$ , the resultant limitation is

$$\bar{x} \ll \epsilon x_0 / (1 - \epsilon), \quad (3.3)$$

which is very restrictive for a spreading drop, because  $\epsilon \ll 1$ . Along with (3.1), the inequality (3.3) is equivalent to the condition

$$h_{(0)} \gg h_N, \quad h_N = \epsilon^{-2} t^{1-2\epsilon}, \quad (3.4)$$

where  $h_N$  is the characteristic scale of the film thickness where the flow becomes non-stationary in the system bound to  $x_0$ .

In order to refine the quasi-stationary theory, we examine small deformations of the p-film (3.1) in the plane case. Obviously, this is valid for sufficiently small times  $t$  due to the conditions (3.3) or (3.4) for using the quasi-stationary approach.

Condition (1.4) on the velocity of the wetting line is fulfilled approximately, because the velocity of the point  $x_{*0}$  differs from  $v_0 = \dot{x}$  by

$$\dot{x}_{*0} - \dot{x}_0 = t^{-\epsilon}(1 - \epsilon)/\epsilon. \quad (3.5)$$

according to (3.2).

As long as the condition (3.3) for the quasi-stationary approach is valid, the right side of (3.5) is small. Then we can seek the difference between the film profile from the stationary one (3.1)

$$h = h_{(0)}(1 + h_1 + \dots), \quad (3.6)$$

by assuming that the unknown correction  $h_1$  is small. Then (1.3) gives an equation for  $h_1$ :

$$\frac{\partial h_{(0)}}{\partial t} - x_0 \frac{\partial}{\partial x} h_{(0)} h_1 = \frac{\partial^2 h_1}{\partial x^2} + \frac{1-m}{x_0} \frac{\partial \ln h_{(0)}}{\partial x}, \quad (3.7)$$

where  $m = 1$  or  $0$  in the plane or axisymmetric case, respectively. From the limiting condition on the velocity of the wetting line (1.4) and with a consideration of (3.5) and (3.6), it follows that

$$\frac{\partial h_1}{\partial x} + \frac{h_1}{x_{*0} - x_0} = -\frac{1-\varepsilon}{\varepsilon x_0}, \quad x = x_{*0}. \quad (3.8)$$

From the second condition (1.4) for the correction  $x_1$  to the coordinate of the wetting line  $x_{*0}$ , we obtain approximately that

$$x_1 = x_* - x_{*0}, \quad h_1(x_{*0}) + \frac{\partial h_{(0)}}{\partial x} x_1 = 0$$

and after we substitute (3.1) we obtain

$$x_1 = (x_{*0} - x_0) h_1(x_{*0}). \quad (3.9)$$

As a result, it is sufficient to determine  $h_1$  in order to find the correction  $x_1$  to the length of the film. The solution to Eq. (3.7) has the form

$$h_1 = C \bar{\xi} + \frac{1-m\varepsilon}{2\varepsilon} \bar{\xi} \ln \frac{\bar{\xi}}{\bar{\xi}_*}, \quad \bar{\xi} = \frac{x}{x_0}, \quad x_0 = t^r. \quad (3.10)$$

By determining  $C$  in (3.10) from (3.8), we obtain

$$h_1 = \frac{\bar{\xi}}{2\varepsilon} \left( -\frac{3}{2} + \left(1 + \frac{m}{2}\right) \varepsilon + (1-m\varepsilon) \ln \frac{\bar{\xi}}{\bar{\xi}_*} \right), \quad (3.11)$$

$$\bar{\xi}_* = (x_{*0} - x_0) / x_0.$$

For  $\varepsilon \ll 1$ , the formula for the second-order approximation of  $h_1$  is almost the same in both the plane ( $m = 1$ ) and axisymmetric ( $m = 0$ ) cases. However, if  $\varepsilon$  is finite, the contribution of  $m$  in (3.11) is noticeable. In order that the perturbation  $h_{(0)}$  not grow as  $t \rightarrow 0$ , we must require  $\varepsilon \leq 1/2$ , which limits the relative length  $\bar{x}$  of the film as  $t \rightarrow 0$ . This refines the condition (2.3).

According to (3.11),  $h_{1*}$  grows proportional to the relative length of the film  $\bar{\xi}_*$ . Here moderate values of  $|h_1| \sim h_{(0)}$  are attained even before the inequality (3.3) becomes an equality. Of course, the theory is not suitable for these values of  $h_1$ . The boundary between the applicability of the quasi-stationary theory and of the secondary approximation (the corrections  $h_1$  and  $h_{(0)}$ ) is determined by starting at a condition where the length  $x_{*0} - x_0$  of the film differs greatly from the second approximation, for example by 30%. The corresponding length of the film for  $\varepsilon = 0.1$  is determined from (3.9) and (3.11). The result is a very stringent condition on the applicability of the quasi-stationary theory for the p-film:

$$x_* - x_0 < 0.03x_0, \quad (3.12)$$

where  $x_* - x_0$  is the length of the p-film and  $x_0$  is the radius of the base of the drop.

The stringent limitation (3.12) on the quasi-stationary theory makes it urgent to investigate an essentially transient theory for p-film dynamics.

**1.4. Estimates of the Applicable Region for the Piston Model of Drop Spreading.** If a movable-singularity model is suitable, then according to (3.1) there exists a quasi-stationary section of film, bounded by (3.3) or (3.4), as  $x \rightarrow x_0$ . The characteristic scale for the transient,  $h_N$  (3.4) covers ever larger thicknesses with increasing time. The maximum thickness  $h_{\max}$  (2.8) of the stationary part of the film also grows. The fate of the stationary part of the film is determined by the ratio

$$h_{\max} / h_N \sim t^{-\gamma}, \quad \gamma = \frac{2}{3} \left(1 - \frac{5}{2}\varepsilon\right). \quad (4.1)$$

For a spreading circular drop,  $\varepsilon = 0.1$  and  $\gamma = 1/2$ ; i.e. the ratio (4.1) dies off as  $t^{-1/2}$ . Consequently, the stationary part of the film (in the moving-piston system) ceases to exist at large enough times characterized by a critical time scale  $t_c$ , when  $h_{\max} \sim h_N$ . According to (2.10) and (3.4), the dimensionless critical time  $t_c$  depends on the equivalent drop radius  $R$ . Considering that values  $t \sim 1$  are characteristic in the piston problem and that they "correspond" to a very long p-film, on the order of the radius  $x_0$  of the drop base, it is interesting to specify the corresponding equivalent drop dimension  $R_0$  from (2.10) and (3.4) for  $\varepsilon = 0.1$ :

$$t_c = 1, R_0 = 1.5 \cdot 10^4 \lambda (h_* / \lambda)^{5/3}. \quad (4.2)$$

Here  $R_0$  gives a boundary, where  $t_c > 1$  for  $R > R_0$  and  $t_c < 1$  for  $R < R_0$ .

The critical time scale  $t_c$  is very important for determining the correctness of models for: 1) the dynamic contact angle  $\alpha_0$  of the drop, and; 2) the spherical segment with the angle  $\alpha_0$ , which approximates the inner region of the drop [8]. Actually, for  $t \sim t_c$ , the corresponding scales  $l$  and  $\varepsilon x_0$  (along the  $x$  coordinate) also coincide because  $h_{\max} \sim h_N$ . The scale  $l$  corresponds to the formation region of the dynamic contact angle (to an order of magnitude) or to the transition region from the p-film to the region affected by capillary forces. It is easy to estimate, because the ratio of  $h_{\max}$  to the film thickness  $h_0$  in the center has an order of magnitude of  $h_{\max}/h_0 \sim 2\varepsilon = 0.2$ . This denotes the end of the applicability of the spherical-segment model, because the dynamic contact angle with the p-film only makes sense in the limit as  $h_{\max}/h_0 \rightarrow 0$ , as is clear from [4] and [8].

Thus, as the drop spreads, the quasi-stationary part of the p-film vanishes at almost the same time as the quasi-stationary picture of the inner region becomes inapplicable, and the model of a piston (moving singularity), which "pushes" the p-film, ceases to make sense. The condition for the applicability of all three models as asymptotic solutions is the same:  $t \ll t_c$ .

**1.5. Boundary Condition for the Time-Dependent Equation and the Boundary Layer at the Wetting Line.** For the transient equation of motion

$$\frac{\partial h}{\partial t} = \frac{\partial}{\partial x} \left( \frac{h^3}{3\mu} \frac{\partial}{\partial x} \left( -\sigma \frac{\partial^2 h}{\partial x^2} - \frac{A'}{6\pi h^3} \right) \right), \quad (5.1)$$

the condition on the wetting line ( $h = 0$ ) can be formulated from the asymptote of the equilibrium equation for the analogous case of stationary film flow [5] as  $h \rightarrow 0$ :

$$h \rightarrow 0, \left( \frac{\partial h}{\partial x} \right)^2 - \frac{A'}{6\pi\sigma h^2} = \alpha_e^2 + \dots \quad (5.2)$$

Here  $\alpha_e$  is a constant, equal to the value of the equilibrium contact angle if the surface is not wetted. If the surface is wetted,  $\alpha_e$  is purely imaginary,  $\alpha_e = i \cdot \alpha_*$ . For  $A' = \text{const}$ , we must require that  $\alpha_* \rightarrow 0$  in order for the singularity in  $\partial h/\partial x$  from (5.2) to occur at values of  $h$  much larger than the dimensions of the liquid molecules. If we do not require the second term  $\alpha_e^2$  of the asymptote for  $\partial h/\partial x$  in (5.2) to be degenerate, then the singularity in  $\partial h/\partial x$  does not occur for real values of  $h$ , which are limited from below by the molecular scale.

We now write an asymptotic expansion of  $h$  which is equivalent to (5.2):

$$\frac{h}{h_*} = \sqrt{2|\bar{x}|} \left( 1 - \frac{3}{4}|\bar{x}| + \dots \right), \quad \bar{x} = \frac{x - x_*}{l_* \sqrt{3}},$$

$$h_* = \lambda / \alpha_*, \quad l_* = \lambda / \alpha_*^2, \quad \lambda^2 = A' / 2\pi\sigma.$$

If we substitute this expansion into (5.1), we see that  $\partial h/\partial t$  is of order  $|\bar{x}|^{-1/2}$  as  $\bar{x} \rightarrow 0$ , while the second term in the expansion on the right side of (5.1) is proportional to  $|\bar{x}|^{-1}$ . Consequently the left side of (5.1) is negligibly small as  $|\bar{x}| \rightarrow 0$  and this expansion can indeed become a boundary condition for (5.1). Another reason is that (5.2) is an integral of the equilibrium equation — a particular case of (5.1).

If the  $h^{-2}$  singularity is removed from (5.2) by setting  $A' = 0$ , then the solution to Eq. (5.1) with a moving wetting line does not exist.

If the coefficient  $\sigma$  in (5.1) is assumed negligibly small [condition (1.1)] far from the wetting line  $h = 0$ , then the "reduced" equation (1.3) with  $\sigma = 0$  is valid. Then (5.1) reduces to the equilibrium equation

$$\sigma \frac{\partial^2 h}{\partial x^2} + \frac{A'}{6\pi h^3} = \text{const}, \quad (5.3)$$

in the boundary layer at the wetting line, and the compatibility condition with the solution of (1.3) outside the boundary layer is written as

$$h \rightarrow h_*, |x - x_*|l^{-1} \rightarrow \infty. \quad (5.4)$$

The thickness  $l$  of the boundary layer is found from the linearized problem for (5.3)

$$l = h_*^2/\lambda = l_*. \quad (5.5)$$

The solution of the boundary-layer problem (5.2) and (5.3) has the form  $h\{x - x_*(t)\}$  for which the liquid velocity is constant  $v(x,t) = \dot{x}$  due to the continuity equation inside the boundary layer.

This allows the velocity of the wetting line to be calculated in terms of the velocity  $v$  outside the boundary layer; i.e. from the solution of the "reduced" equation (1.3).

The parameter  $h_*$  is the minimum equilibrium film thickness [5]. In general, the shape of  $h(x)$  cannot be expressed in terms of elementary functions from (5.3). However, the form of a semi-infinite film of minimum thickness is elementary:

$$X = \ln \frac{1}{1-Y} + 2 \ln \frac{\sqrt{3} + \sqrt{1+2Y}}{\sqrt{3} + 1} + \sqrt{3}(1 - \sqrt{1+2Y}),$$

$$X = (x_* - x)/l_*, \quad Y = h/h_*.$$

From this it is easy to estimate the scale of localizations in the solution. For  $X = 1$ , we have  $Y = 0.8106$ . That is the value of  $l_*$  is in good agreement with the boundary layer thickness, because  $Y = 1$  for  $X = \infty$ .

There is always a boundary layer on the wetting line if the reduced Eq. (1.3) is valid. The reason is that if the inequality (1.1) is fulfilled far from the wetting line, it is all the more true near the wetting line, because  $h_* = \min\{h\}$  in (5.5).

## § 2. ASYMPTOTIC BEHAVIOR OF FILMS SPREADING OVER A SOLID VIA VAN DER WAALS FORCES

**2.1. Exact Solutions of the Transient P-Film Problem.** For the one-dimensional boundary problem we write (1.3), (1.4), (2.1) and (2.2) from § 1 in the dimensionless notation of (2.5) in § 1, but we introduce more general length and time scales,  $X$  and  $T$ , one of which may be taken to be arbitrary:

$$\frac{\partial h}{\partial t} = \Delta \ln h, \quad v = -\frac{1}{h^2} \frac{\partial h}{\partial x}, \quad (1.1)$$

$$h = 1, \quad v = x_*, \quad \text{when } x = x_*; \quad (1.2)$$

$$h \rightarrow \infty, \quad v \rightarrow x_0 \quad \text{when } x \rightarrow x_0;$$

$$X/\sqrt{T} = \sqrt{\kappa}/h_*, \quad \kappa = A'/6\pi\mu. \quad (1.3)$$

For solutions of the type

$$h = y(\xi), \quad \xi = x/\sqrt{2t} \quad (1.4)$$

in the plane case, Eq. (1.1) gives an equation and conditions

$$-\xi y' = (\ln y)'', \quad \xi < \xi_*; \quad (1.5)$$

$$y = 1, y' = -\xi_*, \xi = \xi_* \quad (1.6)$$

The fixed singular point  $x_0 = 0$  corresponds to  $\xi_0 = 0$ . In this case, the asymptotic solution to (1.5) for  $\xi \rightarrow 0$  corresponds overall to the exact solution

$$y = \frac{1}{\xi^2} + \dots, \xi \rightarrow 0. \quad (1.7)$$

Equation (1.5) has the integral

$$\xi y' / y + 2 \ln |y' / y^{3/2}| + \xi^2 y = C, \xi^2 y \neq \text{const} \neq 1, \quad (1.8)$$

which on the asymptote (1.7) is equal to

$$C = 2 \ln 2 - 1. \quad (1.9)$$

Substituting (1.6) and (1.9) into (1.8) gives

$$\xi_* = \sqrt{4/e},$$

from which we obtain an equation of motion of the wetting line

$$\sqrt{t} \frac{dx_*}{dt} = \sqrt{\frac{2}{e}} \quad (1.10)$$

when we consider (1.4).

In dimensional notation (1.10) includes a multiplier (1.3). It is interesting to see how close we can come to the case  $x_0 = 0$  and still realize (1.10), especially when there are no singularities in the solution to (1.5) and (1.6).

**2.2. Spreading of a Semi-Infinite Film.** Let the film have a constant thickness at time  $t = 0$ :

$$h = h_0, x < 0, \quad (2.1)$$

and let this thickness be large ( $h_0 \gg 1$ ). Because  $1/h_0$  is small, the solution can be found by splicing the asymptotes. We examine an auxiliary problem for (1.5) with the condition (2.1) and

$$y = 1/\xi^2 + \dots, \xi \rightarrow \infty. \quad (2.2)$$

By using an invariant transformation, we easily find the dependence of the solution on  $h_0$ :

$$y = h_0 Y(\xi \sqrt{h_0}), \quad (2.3)$$

where  $Y$  is the solution to the problem for  $h_0 = 1$ . In order to complete the information on  $Y$  in (2.3), it is sufficient to show that asymptote of its derivative as  $\xi \rightarrow \infty$ , which follows from (1.5), (1.8), and (2.2):

$$Y'(z) = -(2/\sqrt{e}) \exp(-z^2/2).$$

The solution (2.3) is extended to the other asymptote (2.2) for small  $\xi \sim h_0^{-1/2}$ . Therefore it is valid to splice this asymptote with the solution to the problem (1.5)-(1.7), for which the asymptote for  $\xi \rightarrow 0$  corresponds to (2.2) for small  $\xi$ .

Thus, the shape of the p-film, which is spreading from a "thick" film of thickness  $h_0 \gg 1$  in the region  $\xi \cdot h_0^{1/2} \gg 1$ , differs little from the case of a fixed piston (1.5)-(1.7). That is, the spreading law (1.10) is valid. It is interesting to estimate the order of magnitude of the difference of the spreading behavior from (1.10) caused by a finite  $h_0$ . To do this we use the general form of the solution to Eq. (1.5) close to  $\xi^{-2}$ :



$$y = \xi^{-2}(1 + b_1 \xi^{-\sqrt{2}} + b_2 \xi^{\sqrt{2}} + \dots).$$

The order of magnitude of the constants  $b_1$  and  $b_2$  in terms of the parameter  $h_0$  is known from the composite solution of the first approximation

$$b_1 \sim -(1/h_0)^{\sqrt{2}}, \quad b_2 \sim 1.$$

With this in mind, we now estimate the perturbation of the boundary condition for  $\xi = \xi_*$  as a result of the first approximation as a quantity of order  $b_1$ . The discrepancy in the boundary condition is removed in the second approximation, which gives a correction on the order of  $b_1$ , from which, along with (1.6), we find the order of magnitude of the difference between the wetting velocity and Eq. (1.10):

$$\sqrt{t} dx_*/dt = \sqrt{2/e} + O(h_0^{-\sqrt{2}/2}).$$

In addition we note that the problem of a semi-infinite film for  $x > 0$  is equivalent to the problem with a boundary condition at  $x = 0$  and  $h = \text{const}$ . Therefore it is interesting to examine a more general condition  $h(0,t) \sim t^n$  for which the solution near  $x = 0$  can be sought in the form

$$h = t^n y(\chi), \quad \chi = x t^{(n-1)/2}. \quad (2.4)$$

It is easy to see that due to the universal asymptote  $2t/x^2$ , which is possible in (2.4) for any  $n$ , the method of splicing the asymptotes is as valid for  $n > 0$  as for  $n = 0$ ; and again the spreading formula (1.10) is valid as  $t \rightarrow \infty$ .

The situation is different for  $n < 0$ . The approximate solution, which does not break down the forward structure of the flow near the wetting line  $x_* \sim \sqrt{t}$ , can be constructed only for restricted times, because the scale of the inner solution  $\sim t^{(1-n)/2}$  grows much faster than  $\sqrt{t}$ .

**2.3. Film Spreading if the Piston Moves as  $x \sim \sqrt{t}$ .** Let the singularity move as

$$\begin{aligned} x_0 &= \xi_0 \sqrt{2t}, \quad \xi_0 > 0; \\ y &\rightarrow \infty, \quad \xi \rightarrow \xi_0. \end{aligned} \quad (3.1)$$

Then in a small region around the point  $\xi_0$  the solution (1.5) is represented in the form

$$y = 1/\xi_0(\xi - \xi_0) + (1/2\xi_0^2)\ln(\xi - \xi_0) + C_0 + \dots \quad (3.2)$$

where  $C_0$  is a constant. Overall, (3.2) coincides with the quasi-stationary solution.

As  $\xi_0 \rightarrow \infty$  (the piston moves with a high velocity), it is sufficient to consider the first term of (3.2) and to obtain  $\xi_* - \xi_0 = 1/\xi_0 \ll 1$ ; i.e. the wetting line approaches the piston.

In the limit  $\xi_0 \ll 1$ , we now examine separate solutions with scales  $\xi \sim \xi_0$  and  $\xi \sim 1$  (the outer region). For  $\xi/\xi_0 \rightarrow \infty$  in the inner solution and  $\xi \rightarrow 0$  in the outer solution, the common limit  $y$  is the exact solution  $1/\xi^2$ . We find the constant  $C_0$  in (3.2) by using (1.8) and the invariant transformation of Eq. (1.5):

$$\xi_0^2 C_0 = -(1/2)\ln \xi_0 + \ln 2 - 5/4, \quad \xi_0 \rightarrow 0.$$

The outer solution ( $\xi \gg \xi_0$ ) coincides with the solution of the problem (1.5)-(1.7), which is valid for  $\xi_0 = 0$ . That is, Eq. (1.10) is satisfied.

Thus, the limiting equation of motion (1.10) of the wetting line, which is infinitely far away from the piston ( $\xi_*/\xi_0 \rightarrow \infty$ ) is fulfilled in the limit as  $\xi_0 \rightarrow 0$ , when the velocity of the piston (3.1) drops off.

**2.4. P-Film Dynamics for a Slow-Moving Piston ( $x_0 = t^\varepsilon$ ,  $\varepsilon \ll 1$ ).** The parameter  $\varepsilon = 0.1$  is rather small for spreading circular drops ( $\varepsilon = 1/7$  for the plane case) [8]. The piston problem for  $\varepsilon \ll 1$  and for times  $t \gg t_0 = \varepsilon^{2/(1-2\varepsilon)}$  allows the use of the method of splicing asymptotes. In a sufficiently small neighborhood of the piston, we seek a solution in the form

$$\begin{aligned}
h &= t^{1-2\varepsilon} y(x/t), \quad \xi = x/t^{\varepsilon} \geq 1, \\
y(1 - 2\varepsilon) - \varepsilon y' \xi &= (\ln y)''; \quad y \rightarrow \infty, \quad \xi \rightarrow 1; \\
y \xi^2 &\rightarrow 1, \quad \xi \rightarrow \infty.
\end{aligned}
\tag{4.1}$$

The problem is simplified in the region  $\xi - 1 \gg \varepsilon$ , where to an accuracy of order  $\varepsilon$  the solution to (4.1) is close to

$$y = 2/(\xi - 1)^2, \quad h = 2t/(x - x_0)^2, \tag{4.2}$$

where  $x_0 \approx \text{const}$ , because  $t^\varepsilon$  varies only slightly as  $\varepsilon \rightarrow 0$ . If  $x_0$  is approximated as a constant, the solution (4.2) can be continued to large values of  $x - x_0$  as a function of  $(x - x_0)/\sqrt{2t}$  in accordance with the problem of the fixed piston in Section 1. As a result, the spreading law (1.10) is fulfilled for  $t \gg t_0 \ll 1$ , which is possible if the length of the p-film is small ( $x_* - x_0 \ll x_0$ ). That  $t_0 \ll 1$  is convenient because of the limitation of the piston model (1.1) and (1.2) to times  $t < t_c$  (Section 1.4).

**2.5. P-Film Spreading in the Lagrange Description.** By using the Lagrange approach to the Stefan problem [9, 10], we transform the relationship in (1.1) to the Lagrange variable  $\zeta$  in the form

$$h \frac{\partial x}{\partial \zeta} = 1, \quad \frac{\partial x}{\partial t} = v = -\frac{1}{h} \frac{\partial h}{\partial \zeta},$$

from which it follows that

$$\frac{\partial Y}{\partial t} = \frac{\partial^2}{\partial \zeta^2} \ln Y, \quad Y = \frac{1}{h}. \tag{5.1}$$

The boundary conditions (1.1) and (1.2) transform to

$$Y = 1, \quad \zeta = 0; \tag{5.2}$$

$$v = \frac{\partial \ln Y}{\partial \zeta} \rightarrow \frac{dx_0}{dt} = \varepsilon t^{\varepsilon-1}, \quad \zeta \rightarrow -\infty. \tag{5.3}$$

The specification of the condition (5.3) at  $-\infty$  is related to the existence of the quasi-stationary solution  $h \sim (x - x_0)^{-1}$  as  $x \rightarrow x_0$ , for which  $\int h \cdot dx$  converges.

As  $t \rightarrow \infty$ , we keep in mind that the scale  $\zeta_1$  in (5.3) differs greatly from the scale  $\zeta_2$  in (5.1) and (5.2):

$$\zeta_1 \sim t^{1-\varepsilon}/\varepsilon, \quad \zeta_2 \sim \sqrt{t}.$$

Obviously  $\zeta_2 \ll \zeta_1$  for  $t \gg t_0 = \varepsilon^{2/(1-2\varepsilon)}$ .

The solution in the region of large  $\zeta_1$

$$Y = t^{2\varepsilon-1} \Phi(\eta), \quad \eta = \zeta t^{\varepsilon-1} \tag{5.4}$$

is found from the boundary problem

$$\begin{aligned}
(2\varepsilon - 1)\Phi + \eta(\varepsilon - 1)\Phi' &= (\ln \Phi)'', \quad \eta < 0; \\
\eta^2 \Phi &= 2 + \dots, \quad \eta \rightarrow 0; \quad (\ln \Phi)' \rightarrow \varepsilon, \quad \eta \rightarrow -\infty.
\end{aligned}
\tag{5.5}$$

As an example, we write the solution of (5.5) as  $\varepsilon \rightarrow 0$ :

$$1/\Phi = e^{-\eta} \int_0^\eta \eta e^{\eta} d\eta.$$

In the region of small  $\zeta_2$  the problem is also self-similar:

$$\begin{aligned}
Y &= y(\xi), \quad \xi = \zeta/\sqrt{2t}; \\
-\xi y' &= (\ln y)'', \quad \xi < 0; \quad y = 1, \quad \xi = 0; \\
y &= 1/\xi^2 + \dots, \quad \xi \rightarrow -\infty.
\end{aligned}
\tag{5.6}$$

The last condition allows the splicing of the solutions (5.5) and (5.6). By using the integral of (1.8), we find from (5.6) that

$$y'(0) = \sqrt{4/e},$$

from which (1.10) is obtained. The agreement is not a coincidence, because (5.6) corresponds to the Lagrangian formulation of the problem of a drop spreading from a fixed singularity.

This solution extends Section 2.4, because the time  $t_0$  when the scales of the inner and outer regions coincide can be seen explicitly, and the structure of the solution is explicit for  $t \gg t_0$ , when these scales differ greatly, and the asymptotic solution is justified. This confirms the earlier conclusion on the function  $x_*(t)$  on the asymptote (1.10).

**2.6. Film Spreading in the Axisymmetric Case.** We now examine the axisymmetric case for a piston that expands as  $\sqrt{t}$  (3.1). Equation (1.1) in the notation of (1.4), where  $x$  is the radius, gives a boundary problem for the equation

$$-\xi^2 y' = (\xi y' / y)' \tag{6.1}$$

with conditions (1.6). Equation (6.1) has the integral

$$\xi^2 y / 2 = q - \ln q + C, \quad q = -\xi y' / 2y, \quad \xi^2 y \neq \text{const.} \tag{6.2}$$

The general solution to Eq. (6.1) is obtained by using the second relation that follows from (6.1) and (6.2)

$$\ln \xi = -\int \frac{dq}{2q(q - \ln q + C)}. \tag{6.3}$$

If  $q$  is viewed as a parameter, then (6.2) gives  $\xi(q)$ , and (6.3) gives  $y(q)$ . From the conditions on the wetting line we find the constant in (6.2) and (6.3)

$$C = \ln q_*, \quad q_* = \xi_*^2 / 2. \tag{6.4}$$

By satisfying the condition  $q \rightarrow \infty$  as  $\xi \rightarrow \xi_0$  at the piston, we obtain the basic equation

$$\ln \frac{\xi_*}{\xi_0} = \int_0^\infty \frac{dq}{2q(q - \ln(q/q_*))}, \tag{6.5}$$

from (6.3) and (6.4), which determines the ratio of the coordinates of the wetting line and the piston  $\xi_*/\xi_0$  as a function of the coefficient in the equation of motion of the wetting line  $x_*^2 = 4q_*$ .

The limiting equation of motion of the wetting line

$$\xi_*^2 = 2/e, \quad x_*^2 = (4/e)t. \tag{6.6}$$

comes from the condition for eliminating a singularity in the integral (6.5)

As  $q_* \rightarrow 1/e$ , according to (6.5),  $\xi_*/\xi_0 \rightarrow \infty$ , i.e. the piston is infinitely far away from the wetting line, and the piston expansion velocity is negligibly small compared to the wetting line velocity. It is important that the limiting spreading equation for the axisymmetric film (6.6) be close to the limiting equation in the plane case (1.10). The difference in the limiting velocity coefficients is a factor of  $\sqrt{2}$ .

It is interesting to determine the convergence rate of the coefficient  $q_*$  to its limit as  $\xi_*/\xi_0$  increases. To do this we write the asymptote of (6.5) as  $q_* \rightarrow 1/e$ , by initially transforming the integral to a form more convenient for calculations:

$$\ln \frac{\xi_*}{\xi_0} = \int_0^\infty \frac{ds}{2(\exp(s - s_*) - s)} = \frac{\pi/\sqrt{2}}{\sqrt{1 - s_*}} - 1.555 + \dots, \quad s_* = -\ln q_*. \tag{6.7}$$

It is convenient to solve (6.7) for  $q_*$ :

$$\frac{\xi_*^2}{2} = q_* = \exp\left(-1 + \frac{\pi^2/2}{\ln^2(4.74\xi_*/\xi_0)}\right). \quad (6.8)$$

Equation (6.8) shows how very slowly  $q_*$  approaches the limit  $1/e$ . For example for  $\xi_*/\xi_0 = 50$ , the difference is close to 20%, for  $\xi_*/\xi_0 = 10$  it is close to 40%. Equation (6.8) is applicable all the way to  $\xi_*/\xi_0 = 2.5$ , where the error does not exceed 10%. The unusually slow approach to the limiting Eq. (6.6) makes it difficult to observe it experimentally, and the coefficient in the spreading equation will be even closer to the plane case (1.10) because the difference should generally be of low importance for limiting  $\xi_*/\xi_0 < 10$ .

The real sense of the piston model ( $x_0 \sim \sqrt{t}$ ) can be confirmed by solving the problem of a slowly expanding piston, which corresponds to a spreading drop.

**2.7. Axisymmetric Problem of P-Film Dynamics for a Spreading Drop** ( $x_0 = t^\varepsilon$ ,  $\varepsilon \ll 1$ ). We briefly examine the structure of the approximate solution for  $t \rightarrow \infty$  in Euler coordinates. In the axisymmetric case Eq. (1.1) transforms to the equation for the plane problem with a corresponding choice of variables:

$$\frac{\partial H}{\partial t} = \frac{\partial^2}{\partial z^2} \ln H, \quad H = x^2 h, \quad z = \ln x \quad (7.1)$$

where  $x$  is the radius. The solution is constructed by using the asymptotic splicing method for  $z_* \rightarrow \infty$ . Near the piston ( $z_0 = \varepsilon \cdot \ln t$ ), the function  $H$  has the approximate form

$$H = 2t/(z - z_0)^2 + \dots, \quad \varepsilon \ll z - z_0 \leq 1. \quad (7.2)$$

In the intermediate range [ $1 \ll (z - z_0) \ll z_*$ ], the solution is found by using time-dependent coordinates:

$$H = 2t\pi^2(z_* - z_0)^{-2} \sin^{-2}((z - z_0)\pi/(z_* - z_0)). \quad (7.3)$$

If  $z_0$  and  $z_*$  are fixed, (7.2) and (7.3) are the exact solutions to (7.1). The splicing of Eq. (7.3) to (7.2) is easily verified.

We note that

$$\min H = 2t\pi^2/(z_* - z_0)^2. \quad (7.4)$$

follows from (7.3).

If  $z - z_0 \gg 1$ , (7.3) is spliced to the self-similar solution (6.2) and (6.3) for  $\xi_0 \rightarrow 0$ . As a result we obtain the limiting equation of motion of the wetting line (6.6).

Thus, in the limit  $\ln t \rightarrow \infty$  ( $z_* \rightarrow \infty$ ), the asymptotic solution of Eq. (7.1) consists of approximate solutions in three regions. Besides (7.2), (7.3), and the self-similar solution for  $z - z_0 \gg 1$ , there is also a traditional region of quasi-stationary film flow at a small distance from the piston  $z - z_0 \ll \varepsilon$ .

It is interesting to find the next term in the asymptote which corrects (6.6). The easiest way to do this is to use the Lagrange approach to the Stefan problem [9, 10].

**2.8. Axisymmetric Drop Spreading in Lagrange Coordinates.** By introducing the Lagrange coordinate  $\zeta$ , we write

$$xh \frac{\partial x}{\partial \zeta} = 1, \quad \frac{\partial \ln x}{\partial t} = -\frac{1}{h} \frac{\partial h}{\partial \zeta}$$

in the axisymmetric case, where  $x$  is the radius. Equations (1.1) and (1.2) are transformed to the previous one for  $Y = (x^2 h)^{-1}$ :

$$\begin{aligned} \frac{\partial Y}{\partial t} &= \frac{\partial u}{\partial \zeta}, \quad u = 2Y + \frac{\partial \ln Y}{\partial \zeta}, \quad \zeta < 0; \\ \frac{\partial \ln Y}{\partial t} &= -2u, \quad \zeta = 0; \quad u \rightarrow \frac{d \ln x_0}{dt}, \quad \zeta \rightarrow -\infty. \end{aligned} \quad (8.1)$$

Transforming (8.1) to new variables

$$Y = t^{-1}\Phi(\eta, \tau), \quad \eta = \xi/t, \quad \tau = \ln t$$

for  $x_0 = t^\varepsilon$  gives

$$\frac{\partial \Phi}{\partial \tau} = \frac{\partial U}{\partial \eta}, \quad U = (2 + \eta)\Phi + \frac{\partial \ln \Phi}{\partial \eta}, \quad \eta < 0; \quad (8.2)$$

$$\frac{1}{\Phi} \frac{\partial \Phi}{\partial \tau} = 1 - 2U, \quad \eta = 0; \quad \frac{1}{\Phi} \frac{\partial \Phi}{\partial \eta} \rightarrow \varepsilon, \quad \eta \rightarrow -\infty.$$

The piston problem with  $\varepsilon = 1/2$  has a second solution, which follows from (8.2):

$$1/\Phi = 2\eta + Ee^{-\eta^2}, \quad E = \text{const.} \quad (8.3)$$

The condition for the absence of singularities for  $\eta < 0$  is that  $E > 4/e$ , which yields (6.6) as  $E \rightarrow 4/e$ .

For  $\varepsilon \ll 1$ ,  $\tau \rightarrow \infty$ , and  $\eta < -2$ , we seek a solution close to the singular solution that corresponds to  $E = 4/e$ . If  $\Phi$  is large at the point  $\eta = -2$ , as in (8.3) for  $E \rightarrow 4/e$ , then the solution to (8.2) in the zeroth approximation is easily specified in the regions  $\eta < -2$  and  $\eta > -2$  under the following conditions

$$\begin{aligned} \eta \rightarrow -\infty, \quad \partial \ln \Phi / \partial \eta \rightarrow \varepsilon; \quad \eta = 0, \quad U = 1/2; \\ \eta + 2 \rightarrow \pm 0, \quad \Phi = 2(\eta + 2)^{-2} + \dots \end{aligned}$$

Thanks to the conditions at  $\eta = 0$  and  $\eta = -\infty$ ,  $\max \Phi$  should grow slowly as  $\tau \rightarrow \infty$ . Obviously the characteristic scale for a change in  $\Phi$  is  $\tau$ . It is important that the time derivatives are relatively small in view of the estimate  $\partial \Phi / \partial \tau \sim \Phi / \tau$ .

The solution in the inner region  $|\eta + 2| \ll 1$  can be obtained by using the order-of-magnitude estimate  $U = O(1)$ , which follows from integrating both parts of (8.2) over  $\eta$ :

$$1/\Phi = (1/G + (1/2)(2 + \eta)^2)(1 + O(\eta + 2)) \quad (8.4)$$

where  $G \approx \max \Phi$  for  $G \gg 1$ . The outer solution for  $\eta > -2$  is found from the stationary equation in the neighborhood of the solution to the zeroth approximation:

$$\frac{1}{\Phi} = \frac{2\eta}{1-w} - \frac{4w}{(1-w)^2} + E \exp\left(-\frac{1-w}{2}\eta\right), \quad U = \frac{1-w}{2}. \quad (8.5)$$

The parameters  $w$  and  $\varepsilon$  vary slowly with time, so  $w \ll 1$  in the neighborhood of the limiting solution. The outer solution for  $\eta < -2$  is specified analogous to (8.5).

The value of  $U$  varies mainly due to the transients near the point  $\eta = -2$  and takes limiting values  $U_{\pm}$  for  $(\eta + 2) \cdot G^{1/2} \rightarrow \pm \infty$ . It follows from Eq. (8.2) that

$$\int_{-2-b}^{-2+b} \frac{\partial \Phi}{\partial \tau} d\eta = U_+ - U_- = \frac{1}{2} - \varepsilon - \frac{w}{2} \quad (8.6)$$

where  $G^{-1/2} \ll b \ll 1$ . By substituting (8.4) into (8.6) and calculating the integral, the main approximation is

$$\frac{d\sqrt{G}}{d\tau} = \frac{1-2\varepsilon}{\pi 2\sqrt{2}}. \quad (8.7)$$

From this it is clear that the change the maximum of  $\Phi$  actually corresponds to the slow relaxation of  $G \sim \tau^2$  as  $\tau \rightarrow \infty$ .

The asymptotes for  $E$  and  $w$  can be found from their relationship to  $G$ . If we take (8.5) to the limit  $\eta \rightarrow -2$  and simultaneously hold  $\eta + 2 \gg |w|$ , then splicing with (8.4) gives

$$4\gamma - 12w = 1/G, \quad \gamma = Ee/4 - 1 \ll 1. \quad (8.8)$$

We estimate the transient effects in the outer solution by calculating  $\partial \Phi / \partial \tau$  from the first approximation (8.5) for  $G^{-1/2} \ll \eta + 2 \ll 1$ . According to this, the condition for the transient term  $G \cdot \ln G \ll G$  is fulfilled if  $G \gg 1$  due to (8.7).

From (8.2), (8.5), (8.7), and (8.8), the coordinate of the wetting line is

$$\frac{x_*^2}{t} = \frac{4}{e} \left( 1 + \frac{2\pi^2}{(1-2\epsilon)^2 \ln^2 kt} \right). \quad (8.9)$$

The constant  $k$  corresponds to the integral of (8.7). We note that (8.7) agrees with (7.4).

Comparison of (8.9) with the asymptote of (6.8) of the self-similar piston problem shows that they agree if we juxtapose  $\xi_*/\xi_0$  with the running value of  $\sim t^{0.5-\epsilon}$ .

Thus, in agreement with (6.8), Eq. (8.9) describes the effect of an anomalously slow change in the coefficient in the spreading equation. Continuing Sections 2.4 and 2.5 [which validate (1.10)] to small times in the axisymmetric case shows the approximate validity of (1.10) for longer times, when the length of the p-film is comparable with the inner region of the drop ( $x_* - x_0 \sim x_0$ ). The reason is that the coefficient in Eq. (1.10) is higher than the analogous coefficient in the axisymmetric limiting equation by a factor of  $\sqrt{2}$  overall. And, by assuming a monotonic change in the spreading coefficient [it is monotonic in (8.9) and (6.5)], the spreading coefficient  $q_*$ , due to its small change, is found to remain closer to the plane case than to the axisymmetric limiting value while the length of the p-film is comparable to the radius of the inner drop region.

**9. Film Spreading Considering Retarded Interaction.** If the thickness  $h \sim 10^{-7}$  m, the contribution of intermolecular forces changes from  $h^{-3}$  to  $h^{-4}$  (the retardation effect of the van der Waals interaction). In order to include this, we use a very simple model of the function  $p(h)$ , in which the exponent changes from  $-3$  to  $-4$  at the point  $h_+$ , so that in the dimensional form

$$p(h) = -A'h_+ / 6\pi h^4, \quad h > h_+.$$

Correspondingly, in Lagrange coordinates instead of (5.1) we have

$$\begin{aligned} \frac{\partial Y}{\partial t} &= \frac{\partial^2}{\partial \zeta^2} \ln Y, \quad Y > Y_+, \quad Y = \frac{1}{h}, \\ \frac{\partial Y}{\partial t} &= \frac{1}{Y_+} \frac{\partial^2 Y}{\partial \zeta^2}, \quad Y < Y_+. \end{aligned} \quad (9.1)$$

The condition on the wetting line  $\zeta = 0$  coincides with (5.2). Conditions at  $h = \infty$ , as opposed to (5.2), are specified, not at  $-\infty$ , but at an unknown moving point:

$$\zeta = \zeta_0, \quad \frac{1}{Y_+} \frac{\partial Y}{\partial \zeta} = \frac{dx_0}{dt} = \frac{\epsilon}{t^{1-\epsilon}}, \quad Y = 0. \quad (9.2)$$

Condition (9.2) means that new Lagrangian particles are created at  $h = \infty$ .

The solution to (5.2), (9.1), and (9.2) is found rather simply while retardation only affects the stationary part of the solution at large values of  $h$ , because in the region  $Y > Y_+$  the problem hardly differs from the case without retardation. The quasi-stationary approximation in the region  $Y \sim Y_+$  falls apart when the transient scale  $h_N \geq h_+$ , which is equivalent to the inequality

$$\epsilon^{-2} Y_+ t^{1-2\epsilon} \geq 1. \quad (9.3)$$

This condition can be satisfied if the drop is sufficiently circular. For example, from (4.2) of § 1, we can find that for  $h_* \sim 2\lambda$ , the values of the equivalent drop radius must be  $R > 10^{-2}$  cm for the retardation of the interaction to affect the film shape; while 1)  $t < t_c$ , and 2) the moving-singularity model is satisfactory at the edge of the film.

Because it is important in principle to determine the retardation effect on p-film spreading, we turn to the most interesting case, where transient effects are substantial and therefore the left side of (9.3) is large. The solution is simplified if we assume  $Y_+ \ll 1$  (values  $Y_+ \sim 0.01$  are possible).

We now use a new variable  $\xi = \zeta/\sqrt{2t}$ ; then Eq. (9.1) takes the form

$$\begin{aligned} 2t \frac{\partial Y}{\partial t} - \xi \frac{\partial Y}{\partial \xi} &= \frac{\partial^2}{\partial \xi^2} \ln Y, \quad Y > Y_+; \\ 2t \frac{\partial Y}{\partial t} - \xi \frac{\partial Y}{\partial \xi} &= \frac{1}{Y_+} \frac{\partial^2 Y}{\partial \xi^2}, \quad Y < Y_+; \end{aligned} \quad (9.4)$$

$$\xi = \xi_0, \frac{\partial Y}{\partial \xi} = \varepsilon \sqrt{2} Y_+ t^{-1/2}, Y = 0; \xi = 0, Y = 1.$$

We seek the asymptote of  $Y$  as  $t \rightarrow \infty$  in the region of the self-similar (i.e. stationary) solution of Eqs. (9.4). We attempt to consider the boundary condition at  $\xi = \xi_0$  parametrically, by assuming small transient terms  $2t \cdot \partial Y / \partial t$  in Eqs. (9.4). Here the problem is evaluating the smallness of the discarded terms in the last estimate in the parametric solution.

By introducing the unknown  $\xi_+$  [ $Y(\xi_+) = Y_+$ ] and by making the approximation

$$\partial Y / \partial \xi = F \exp(-\xi^2 Y_+ / 2),$$

for  $\xi \in (\xi_0, \xi_+)$ , we obtain from (9.4) that

$$\begin{aligned} -Y_+ &= F \int_{\xi_+}^{\xi_0} \exp(-\frac{\xi^2}{2} Y_+) d\xi, F \exp(-\frac{\xi_0^2}{2} Y_+) = \frac{Y_+ \varepsilon \sqrt{2}}{t^{0.5-t}}, \\ \xi &= \xi_+, \partial Y / \partial \xi = F \exp(-\xi_+^2 Y_+ / 2). \end{aligned} \quad (9.5)$$

The first and third Eqs. (9.5) can be examined independently of the second by seeking  $F$  and  $\xi$  as a function of  $\xi_0$ . The completion of the problem is simplified if  $|\xi_+| \gg 1$ . In this case an intermediate asymptote of the solution is possible:

$$Y = 1/\xi^2 + \dots, |\xi_+| \gg |\xi| \gg 1. \quad (9.6)$$

By determining the constant in the integral (1.8) according to (9.6), we have from (1.8) and (9.5) that

$$\begin{aligned} \theta^2 - \theta \psi + 2 \ln \psi &= 2 \ln 2 - 1, \\ \frac{1}{\psi} &= e^{\theta^2/2} \int_{\theta}^q e^{-\theta^2/2} d\theta, \psi = \frac{Y'(\xi_+)}{Y_+^{3/2}}, \\ \theta &= -\xi_+ \sqrt{Y_+}, q = -\xi_0 \sqrt{Y_+}. \end{aligned} \quad (9.7)$$

As  $q \rightarrow \infty$ , the solution to (9.7) is found explicitly after some simple calculations:

$$\theta = 1.093 - (1.02/q) e^{-q^2/2}, \psi = 1.603. \quad (9.8)$$

It follows from (9.6)-(9.8) that

$$F = 2.91 Y_+^{3/2}, \xi_0^2 = \frac{q^2}{Y_+} = \frac{1}{Y_+} \ln \left( \frac{Y_+ t^{1-2\varepsilon}}{0.236 \varepsilon^2} \right). \quad (9.9)$$

As expected, the value of  $\xi_0$  grows slowly as  $t \rightarrow \infty$  according to (9.9).

By determining  $d\xi_+/d\xi_0$  from (9.8), we find the time derivatives  $\dot{\xi}_+$ ,  $\dot{F}$ , and  $\dot{\xi}_0$ ; as a result of direct calculations for  $\xi < \xi_+$  we obtain

$$2t \left| \frac{\partial Y}{\partial t} \right| / \left| \xi \frac{\partial Y}{\partial \xi} \right| = O\left(\frac{1}{q^2}\right). \quad (9.10)$$

Evaluation of (9.10) as  $q \rightarrow \infty$  confirms the consistency of the approximate solution, including the validity of (9.6).

From (1.8) and (9.6) we obtain  $Y_{\xi'} = \sqrt{4/\varepsilon}$  at  $\xi = 0$ , which corresponds to Eq. (1.10) without considering retardation. Consequently, the spreading equation (1.10) remains valid if retardation is important in a region of large thicknesses.

We note the essential role of the Lagrange description of the Stefan problem [9, 10] for obtaining the approximate solution of the non-self-similar problem considering retardation.

Thus, the equation of motion of the wetting line for a film spreading from a fixed piston (Section 2.1) is asymptotic for a whole series of fundamental problems (Sections 2.2-2.9) for the spreading of thin films. Consequently the function  $v_* \sqrt{t} = \text{const}$  (1.10) is universal in a very definite sense.

We note that a spreading equation coefficient which is found experimentally can serve as a source for additional information on van der Waals forces in the boundary condition for wetting.

## REFERENCES

1. Yu. S. Barash, Van der Waals Forces [in Russian], Nauka, Moscow (1988).
2. O. V. Voinov, "Wave motions in a viscous liquid layer in the presence of surface-active materials," *Prikl. Mekh. Tekh. Fiz.*, No. 3, 81-89 (1971).
3. C. Huh and L. E. Scriven, "Hydrodynamic model of a solid/liquid/fluid contact line," *J. Colloid Int. Sci.*, **35**, No. 1, 85-101 (1971).
4. O. V. Voinov, "Boundary slope angles in moving liquid layers," *Prikl. Mekh. Tekh. Fiz.*, No. 2, 92-99 (1977).
5. H. Hervet and P. G. deGennes, "The dynamics of wetting of a 'dry' solid," *Compt. Rend. Acad. Sci. Paris, Series II*, **299**, No. 9, 499-503 (1984).
6. J. Lopez, C. A. Miller, and E. Ruckenstein, "Spreading kinetics of liquid drops on solids," *J. Colloid Int. Sci.*, **56**, No. 3, 460 (1976).
7. W. D. Bascom, R. L. Cottington, and C. R. Singletary, "Dynamic surface phenomena in the spontaneous spreading of oils on solids," *Contact Angles, Wettability, and Adhesion*, (E. W. Fowkes, ed.), American Chemical Society, Washington, DC (1964).
8. O. V. Voinov, "Hydrodynamics of wetting," *Izv. Akad. Nauk, Mekh. Zhidk. Gaza*, No. 5, 76-84, (1976).
9. A. M. Meirmanov and V. V. Pukhnachev, "Lagrangian coordinates in the Stefan problem," *Dynamics of Solids: A Collection of Scientific Works*, Institute of Hydrodynamics, Academy of Sciences, Siberian Division (1980), Vol. 47, pp. 90-111.
10. V. V. Pukhnachev, "Transformations of equivalence and the hidden symmetry of time-dependent equations," *Dokl. Akad. Nauk*, **294**, No. 3, 535-538 (1987).