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CLOSURE OF THE HYDRODYNAMIC THEORY OF WETTING IN A SMALL-SCALE REGION

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The shape of the free boundary in the wetting of a smooth surface of a solid by a polymer liquid is investigated with allowance for the possible existence of a flow region exhibiting anomalous viscosity. An analytical solution of the problem is obtained for the rheological model of a nonlinearly viscous fluid in the thin-layer or film approximation, and it is compared with the solution for a weak dependence of the viscosity on the shear rate. An equation, invariant under the degree of polymerization (D.P.) of the polymer molecules, is derived for the scale of the region of the viscosity anomaly. It is shown that the rheological treatment makes sense only for sufficiently large values of the macroscopic contact angle. Equations are found for the minimum admissible dynamic contact angles and capillary numbers limiting the validity of the rheological approach to closure of the theory in a small-scale region.

The theory is compared with experimental work on capillary wetting. Allowance for the rheology of the liquid is effective in describing only part of the experimental dependence of the contact angle on the velocity. In the range of parameters where the theory taking rheology into account is valid, its results agree almost exactly with the results obtained for a Newtonian fluid. Similar agreement has been noted previously for the spreading of a polymer liquid droplet on a solid surface.

1. DYNAMIC CONTACT ANGLE OF A NONLINEARLY VISCOUS LIQUID ON A SOLID SURFACE

We consider the planar, steady flow of a liquid with a free boundary S, which moves with a velocity v relative to the solid wetted by it (Fig. 1). The Reynolds number is assumed to be small.

The standard formulation of the theory of wetting [1, 2] on a solid stipulates the no-slip condition $v_x = -v$, $v_y = 0$ at $y = 0$, along with the conditions on the free boundary S: impermeability of the liquid and zero tangential stresses

$$\mathbf{v}\cdot\mathbf{n} = 0,\ p_\tau = 0$$

and equality between the jump of the normal stress and the capillary pressure

$$p_n + p_0 = q\sigma.$$

Here q is the curvature of the surface S, p_0 is the pressure in the gas, and σ is the coefficient of surface tension.

We also assume that the values of the velocity v are specified and continuous on the arcs L_0 and L_m of the circles of large and small radius passing through points of the free boundary at distances h_0 and h_m from the solid surface ($h_0 >> h_m$). For definiteness, the centers of these circles are located at the intersections of the corresponding tangents to the free boundary S with the boundary of the solid $y = 0$.

The dependence of the angle α of the tangent to S relative to the solid surface on the distance h of a point of S from the solid surface is determined in the intermediate range

$$h_m \ll h \ll h_0,$$

where the values of the velocity on the large and small bounding arcs L_0 and L_m do not influence of the flow in the intermediate range of distances h, provided that they are both of the same order of magnitude as the wetting rate v.

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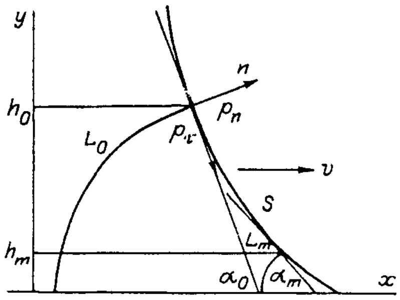

Fig. 1

The order of magnitude of the minimum distance h_m is specified [1, 2] to as two or three molecular diameters [$h_m = (2\text{-}3)a$]. The angle α at the minimum distance h_m is set equal to the static contact angle:

$$\alpha = \alpha_m, \quad h = h_m. \tag{1.1}$$

We assume that the capillary number is small: $\mathrm{Ca} = \mu_0 v/\sigma \ll 1$, where μ_0 is the maximum viscosity of the liquid. We also assume that the curvature q at the point h_0 of the free boundary decreases rapidly:

$$q(h_0) = -\left.\frac{d\cos\alpha}{dh}\right|_{h_0} \to 0. \tag{1.2}$$

The rheological equation of state of the liquid is written as the equation of a nonlinearly viscous fluid: The stresses p_{ij} are determined by the viscosity μ, which decreases monotonically at large shear rates $\gamma^\cdot$:

$$p_{ij} = -p\delta_{ij} + 2\mu\varepsilon_{ij}, \quad \varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial v_i}{\partial x_j} + \frac{\partial v_j}{\partial x_i}\right), \quad i, j = 1, 2, 3,$$

$$\mu = \mu(\gamma^\cdot), \quad \gamma^\cdot = (2\varepsilon_{ij}\varepsilon_{ij})^{1/2}.$$

These expressions are model equations for a polymer liquid, since they do not take the effect of normal stresses into account.

Of special interest in regard to an approximate analytical description is the class of viscosity — shear rate functions $\mu(\gamma^\cdot)$ having a slow rate of change of the viscosity with the shear rate [1]:

$$\mu \gg \gamma^\cdot \left|\frac{d\mu}{d\gamma^\cdot}\right|.$$

This inequality is satisfied, for example, by a power-law function $\mu \sim \gamma^{\cdot\,-k}$ with a small power exponent ($k \ll 1$). An analytical solution is also possible when the tangent to the free boundary forms a small angle relative to the solid surface (i.e., in the case of a thin layer).

The slow variation of the viscosity with the shear rate means that the solution of the problem of flow of a liquid of constant viscosity within the angle α can be used to solve the nonlinear problem of the shape of the free boundary if the angle α of the tangent varies slowly with the distance h, i.e., if

$$\alpha \gg h\,|d\alpha/dh|.$$

This inequality can be satisfied by virtue of the small capillary number ($\mathrm{Ca} \ll 1$).

If we introduce a characteristic shear rate in a flow region having a scale h equal to the distances from the solid surface

$$\gamma^\cdot = \varkappa\frac{v}{h}, \tag{1.3}$$

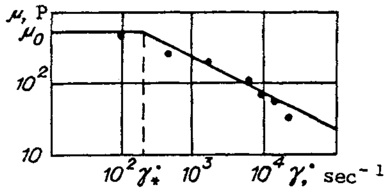

Fig. 2

we can determine the viscosity μ in this region and calculate the difference of the normal stresses at the boundary from the corner flow problem. We can then use the method of [1] to obtain the asymptotic dependence of α on h from the differential equation for the angle α, which gives an expression for the curvature. For $\alpha < 145\text{-}150^\circ$ this dependence can be described by the approximate relation

$$\alpha^3 = \alpha_m^3 + \frac{9v}{\sigma}\int_{h_m}^{h} \mu\left(\varkappa\frac{v}{h}\right)\frac{dh}{h}. \tag{1.4}$$

An order-of-magnitude determination of the characteristic value of $\varkappa$ is sufficient in Eqs. (1.3) and (1.4), because the viscosity μ is assumed to depend only slightly on $\gamma^{\boldsymbol\cdot}$. The foregoing analysis of the wetting of a surface by a thin liquid layer shows that a good approximation is achieved with $\varkappa = 2$. In [1] the value of $\varkappa$ differs by the additional factor α^{-1}.

We should mention the more general asymptotic equation from which Eq. (1.4) is deduced:

$$\int_{\alpha_m}^{\alpha}\left(\frac{\beta}{\sin\beta} - \cos\beta\right)d\beta = \frac{2v}{\sigma}\int_{h_m}^{h}\mu\left(\varkappa\frac{v}{h}\right)\frac{dh}{h}. \tag{1.5}$$

The applicability of this equation is limited by the requirement of moderate slopes ($\alpha \lesssim \pi/2$) in the range of distances h where the viscosity anomaly occurs. This limitation is imposed by the fact that $\gamma^{\boldsymbol\cdot}$ (1.3) is not a characteristic shear rate in a region with the scale of distances from the surface equal to h for $\varkappa$ = const and large (close to π) angles α.

Obviously, the integrals with respect to h in Eqs. (1.4) and (1.5) converge for $h_m = 0$ if the viscosity μ decays sufficiently rapidly at large shear rates ($\gamma^{\boldsymbol\cdot} \to \infty$) [3-5]. The case $h_m = 0$ corresponds to the general scheme, analogous to those in standard approaches [6, 7], for continuous closure of the problem for h = 0. It will be shown below, however, that the passage to the limit $h_m \to 0$ is inadmissible in general.

To specify the particular dependence of the viscosity on the shear rate, it is useful to refer to experiments involving siloxane polymer liquids [8, 9], which can be approximately described by power-law dependences of the viscosity μ on the shear rate for values of the latter above the critical value $\gamma^{\boldsymbol\cdot}_*$:

$$\mu = \mu_0 = \text{const}, \quad \gamma^{\boldsymbol\cdot} \leq \gamma^{\boldsymbol\cdot}_*, \quad \mu = \mu_0(\gamma^{\boldsymbol\cdot}_*/\gamma^{\boldsymbol\cdot})^k, \quad \gamma^{\boldsymbol\cdot} > \gamma^{\boldsymbol\cdot}_*. \tag{1.6}$$

As an example, the approximate dependence (1.6) is compared with experiment [9] in Fig. 2 for siloxane liquid with $\mu_0 = 600$ P, where the following parameters are used in Eq. (1.6): $k = 0.5$; $\gamma^{\boldsymbol\cdot}_* = 200$ sec^{-1}.

We transform Eq. (1.4), taking (1.6) into account, for $h \geq h_*$:

$$\alpha^3 = \alpha_m^3 + \frac{9\mu_0 v}{\sigma}\left(\ln\frac{h}{h_*} + \Gamma\right), \quad \Gamma = \frac{1}{k}\left(1 - \left(\frac{h_m}{h_*}\right)^{1-k}\right), \quad h_* = \varkappa\frac{v}{\gamma^{\boldsymbol\cdot}_*}. \tag{1.7}$$

One important factor limits the validity of using Eqs. (1.4), (1.5), and (1.7) to take into account the rheology of the liquid outside a small region of scale h_m, namely the condition that the scale of the viscosity anomaly region is much greater than the molecular scale ($h_* \gg h_m$). We note that the expression for Γ in (1.7) can be used to estimate the order of magnitude of the contribution of the flow conditions on the minimum scale $h \sim h_m$. The formal passage to the limit $h_m/h_* \to 0$ would make it possible to obtain a closed solution on the basis of the closure relation for $h = 0$ without any need to use the conditions at $h = h_m$. However, such a limit is nonexistent, for example, in the case of a relatively small wetting rate ($v \to 0$), when $h_* \to 0$. It is therefore important to determine the conditions under which the inequality $h_* \gg h_m$ holds, as these conditions govern the validity of the rheological approach to closure of the problem in a small-scale region. In this regard, it is useful to determine the solutions for small slopes of the tangent to the free boundary.

2. EQUATIONS OF CAPILLARY MOTION OF A THIN LAYER WITH ALLOWANCE FOR THE VISCOSITY ANOMALY

The velocity v_x in a thin liquid layer satisfies the equation

$$\frac{\partial}{\partial y}\mu\frac{\partial v_x}{\partial y} = \frac{\partial p}{\partial x},$$

where x is the coordinate along the layer, and y is the coordinate transverse to it. The conditions at the boundaries of the layer with the solid and the gas are

$$v_x = 0,\quad y = 0;\quad \frac{\partial v_x}{\partial y} = 0,\quad y = h.$$

The flow of liquid through a cross section of the film for a power-law dependence of the viscosity on the shear rate (1.6) has the form

$$Q = \int_0^h v_x dy = \frac{\dot{\gamma}_* h^2}{3 - 2k}\left[(1 - k)\,\zeta^{1/(1-k)} + \frac{k}{3}\frac{1}{\zeta^2}\right],\quad \zeta > 1, \tag{2.1}$$

$$Q = \frac{1}{3}\dot{\gamma}_* h^2 \zeta,\quad \zeta \leqslant 1;$$
$$\zeta = -\frac{h}{\mu_0 \dot{\gamma}_*}\frac{\partial p}{\partial x}. \tag{2.2}$$

A more convenient representation of Eqs. (2.1) can be obtained without sacrificing acceptable accuracy. We consider the approximation (2.1) in the form

$$\begin{aligned} Q &= \frac{1 - k}{3 - 2k}\dot{\gamma}_* h^2 \zeta^{1/(1-k)},\quad \zeta > \zeta_*,\\ Q &= \frac{1}{3}\dot{\gamma}_* h^2 \zeta,\quad \zeta < \zeta_*. \end{aligned} \tag{2.3}$$

The parameter ζ_* is determined from the condition of continuity of the flow Q at $\zeta = \zeta_*$:

$$\zeta_* = \left(\frac{1 - 2k/3}{1 - k}\right)^{1/k-1}. \tag{2.4}$$

The equation for the profile of a film in steady flow with a velocity v follows from the equation of continuity in integral form and the capillary pressure equation:

$$Q = hv,\quad p - p_0 = -\sigma\frac{\partial^2 h}{\partial x^2}. \tag{2.5}$$

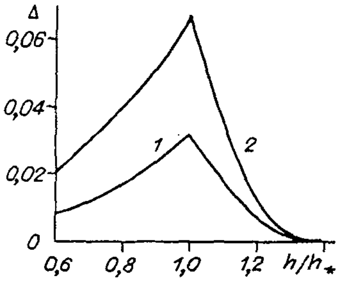

Fig. 3

Equations (2.2)-(2.5) lead to the expressions

$$\frac{d^3h}{dx^3} = \frac{3\mu_0 v}{\sigma h^2}, \quad h > h_*, \quad \frac{d^3h}{dx^3} = \frac{3\mu_0 v}{\sigma h^2}\left(\frac{h}{h_*}\right)^k, \quad h \leqslant h_*,$$
$$h_* = \varkappa v/\dot{\gamma}_*, \quad \varkappa = 3/\zeta_*, \quad \varkappa = 2{,}15 - 2{,}25, \quad k = 0 - 0{,}5. \tag{2.6}$$

The relative error Δ of approximate calculation of the right-hand side of the differential equation (2.6) according to (2.3) and (2.4) in comparison with the calculation according to (2.1) is negligible if the power exponent k is small. This statement is supported by Fig. 3, which shows graphs of the error Δ for k = 0.25 and 0.5 (curves 1 and 2). For k = 0.5 the maximum error is Δ = 6.6%. Here the error of calculation of h by the approximate equations (2.6) does not exceed 1%, owing to the rapid decrease of Δ with increasing deviation of h from h_*.

Using the notation

$$h = yh_*, \quad x = h_*\left(\frac{\sigma}{3\mu_0 v}\right)^{1/3}\xi, \tag{2.7}$$

we can rewrite Eqs. (2.6) in the form

$$y^2y''' = 1, \quad y \geqslant 1,$$
$$y^{2-k}y''' = 1, \quad y < 1. \tag{2.8}$$

For a thin layer we have

$$\alpha = -dh/dx,$$

and the boundary conditions (1.1) and (1.2) assume the form

$$y'' \to 0, \quad y \to \infty, \quad y' = -\alpha_m\left(\frac{\sigma}{3\mu_0 v}\right)^{1/3}, \quad y = \frac{h_m}{h_*}. \tag{2.9}$$

Next we consider the limit $h_* \gg h_m$, whereupon the second boundary condition (2.9) is stipulated at y = 0.

The approximate solution (1.7) can be rewritten with (2.9) taken into account:

$$-y' = (b^3 + 3\Gamma + \ln y)^{1/3}, \quad y \geqslant 1, \quad b^3 = \frac{\alpha_m^3\sigma}{3\mu_0 v}. \tag{2.10}$$

3. ANALYTICAL SOLUTION OF THE BOUNDARY-VALUE PROBLEM FOR LARGE WETTING RATES

At sufficiently high velocities ($\alpha_m^3\sigma \ll 3\mu_0 v$) or for complete static wetting, when the contact angle $\alpha_m = 0$, the second condition (2.9) gives

$$y' = 0, \quad y = 0.$$

We now investigate the asymptotic behavior of the solution of Eq. (2.8) for y > 1 [2]:

$$y' = -(3z)^{1/3}\left(1 - \frac{\ln|z|}{9z} + \ldots\right), \quad z = C + \ln y \to \infty \tag{3.1}$$

(C is a parameter). Denoting by θ the yet-unknown angle (in variables y, ξ) at the boundary of the viscosity anomaly region:

$$y' = -\theta, \quad y = 1, \tag{3.2}$$

from (3.1) we find

$$y'' = \frac{1}{\theta}\left(1 - \frac{1}{\theta^3} + \ldots\right), \quad y = 1. \tag{3.3}$$

We use the subscript (+) to label the solution for y > 1. Including one or two terms, respectively, we then write in accordance with (3.3)

$$y''_{(+)1} = \frac{1}{\theta}, \quad y''_{(+)2} = \frac{1}{\theta}\left(1 - \frac{1}{\theta^3}\right). \tag{3.4}$$

Next we consider the region y < 1, in which Eq. (2.8) is conveniently rewritten

$$u^{1/2}u'' = -2y^{k-2}, \quad u = (y')^2. \tag{3.5}$$

Equation (3.5) in conjunction with the condition y′ = 0 at y = 0 has the exact solution

$$u_0 = c_0^2 y^{2k/3}, \quad c_0 = \left(\frac{9}{k(3-2k)}\right)^{1/3}. \tag{3.6}$$

An approximate solution can be sought in the neighborhood of u_0 in the series form

$$u = u_0 + u_1 + u_2 + \ldots, \quad u_0 \gg |u_1| \gg |u_2|. \tag{3.7}$$

To within an arbitrary constant, the first two terms of the series have the form

$$u_1 = Ay^{k_1}, \quad u_2 = -\frac{A^2}{2c_0^2}\frac{k_1(k_1-1)y^{k_2}}{\frac{1}{3}k\left(\frac{2}{3}k - 1\right) + k_2(k_2-1)},$$
$$k_1 = \frac{1}{2} + \sqrt{\frac{1}{4} + \frac{k}{3}\left(1 - \frac{2k}{3}\right)}, \quad k_2 = 2k_1 - \frac{2}{3}k. \tag{3.8}$$

The following notation is useful:

$$y'_{(-)i} = -\left(\sum_{l=0}^{i-1} u_l\right)^{1/2} . \tag{3.9}$$

According to Eqs. (3.4) and (3.9), the unknown constants θ and A in expressions (3.1) and (3.6)-(3.8) are determined from two equations, specifically the conditions of continuity of the derivatives:

$$y'_{(-)i} = y'_{(+)j}, \quad y = 1, \quad y''_{(-)i} = y''_{(+)j}. \tag{3.10}$$

We denote y′ in (3.10) by $-\theta_{ij}$. Calculations for k = 1/2 show that θ_{22} differs from θ_{32} = 1.955 (Γ = 2.492) by 0.015% in order of magnitude, i.e., the inclusion of the third term in Eq. (3.7) yields excessive accuracy.

The inclusion of only one term in the asymptotic equation (3.1) gives θ_{21} = 1.983 (Γ = 2.6), which differs from θ_{22} at most by 1.4%. Consequently, one term in the asymptotic equation (3.1) permits the boundary-value problem for Eq. (2.8) to be solved within acceptable error limits and to describe the solution correctly for y > 1.

Of special interest is the value of θ_{11}, determined without regard for the second equation (3.10), from the first term of (3.7), which represents the exact solution u_0, where independently of the solution for y > 1,

$$\theta_{11} = \left(\frac{3}{k(1 - 2k/3)}\right)^{1/3} . \tag{3.11}$$

For k = 0.5 the error of the solution θ_{11} = 2.08 is only 6.3%.

It is interesting to assess the efficiency of the solution (1.7) $\theta^3 = 3/k$. For k = 1/2 the error of the value θ = 1.82 corresponding to (1.7) in comparison with the exact calculated value is only 7%. The error is even lower for smaller values of k. Consequently, both of the solutions (1.7) and (3.11) are acceptable for k ≤ 1/2, where the exact value of the angle θ lies approximately midway between them.

4. ASYMPTOTIC JUSTIFICATION OF THE APPROXIMATE ANALYTICAL SOLUTIONS IN THE LIMIT k → 0

The above analytical solutions can be strengthened by analyzing the asymptotic behavior of the solution of the boundary-value problem (2.8), (2.9) in the small-k limit (k → 0), which is determined from Eqs. (3.1)-(3.10) in the form

$$\theta = \left(\frac{3}{k(1 - 2k/3)}\right)^{1/3} \left(1 - \frac{1}{3}k^2 + o(k^2)\right), \quad k \to 0, \quad \theta = -y'|_{y=1}. \tag{4.1}$$

The principal term of the asymptotic equation (4.1) corresponds to the approximate solution obtained for Γ with h_m = 0 in (1.7) on the basis of the principle of slow variation of the angle with the distance h [1] and smallness of the quantity k (k ≪ 1).

Disregarding the term $(1/3)k^2$ in (4.1), we obtain Eq. (3.11), which is asymptotically more accurate than the principal term of Eq. (4.1).

The fact that the efficiency of the approximate analytical solutions of the problem of the angle at the boundary between the viscosity anomaly region and the region of constant viscosity may depend on the coincidence of these solutions with one or two terms of the asymptotic equation (4.1) can be ruled out as a factor in the comparison.

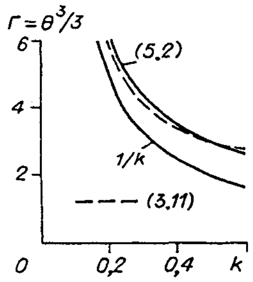

Fig. 4

5. SOLUTION OF THE BOUNDARY-VALUE PROBLEM FOR SMALL WETTING RATES

For large values of the parameter

$$b^3 = \frac{\alpha_m^3 \sigma}{3\mu_0 v} \gg 1$$

the asymptotic behavior of the solution of Eq. (2.8) for $y \ll 1$ can be obtained on the basis of (3.5) in the form

$$y' = -b\left(1 + \frac{2}{b^3(1-k)k} y^k + c_1 y + \ldots\right)^{1/2}, \tag{5.1}$$

where c_1 is an arbitrary constant. The condition for Eq. (5.1) to be valid for $y \leq 1$ and $c_1 \ll 1$ has the form

$$b^3 \gg \frac{1}{k(1-k)}.$$

The asymptotic solution of the boundary-value problem (2.8), (2.9) in the limit $b \to \infty$ with allowance for (3.1), (3.2), and (5.1) can be used to find the angle θ and the value of Γ in (2.10):

$$\Gamma = \frac{1}{3}\theta^3 = \frac{k+1}{k}, \quad b \to \infty. \tag{5.2}$$

The important feature of Eq. (5.2) is its validity for any k. It is instructive to compare it with Eq. (3.11), which is valid for $b = 0$, and with Eq. (1.7). Clearly, the equations coincide in the limit $k \to 0$. The indicated equations are compared for finite k in Fig. 4, from which it is evident that Eqs. (3.11) and (5.2) give practically identical results for θ, which differ at most by 1.3% for $k \leq 1/2$. In the case of Eq. (1.7) the error of $\alpha(h_*)$ does not exceed 14.5%. Consequently, the equation (3.11) obtained for small values of the parameter b also work quite well for large values of this parameter. It is therefore reasonable to expect that it should also apply to intermediate values of $b \sim 1$, i.e., everywhere.

We note that Eqs. (1.7) and (3.11), which are valid for arbitrary values of the parameter b and for $k \leq 1/2$, give upper and lower bounds of the angle α, respectively, but these bounds are close to one another.

The results confirm the efficiency of Eq. (1.7), which has been derived not only for small values, but also for larger finite values of the angles.

6. SCALE EQUATIONS FOR THE REGION OF THE VISCOSITY ANOMALY AND LIMITS OF THE RHEOLOGICAL APPROACH

Polymer liquids having substantially different molecular weights are used in experiments. It is important in this regard to estimate the dependence of the scale of the viscosity anomaly on the molecular weight of the polymer or on the D.P. N (number of structural units in the molecular chain).

It is a well-known fact [8, 10] that the behavior of the maximum relaxation time of a polymer liquid τ with increasing D.P. N is the same as that of the maximum viscosity:

$$\tau \sim N^{3,4}, \quad \mu_0 \sim N^{3,4}.$$

The characteristic critical shear rate has the value $\dot{\gamma}_* \sim 1/\tau$, so that the critical stress p_* does not depend on the D.P. N:

$$\mu_0 \dot{\gamma}_* = p_* = \text{const.} \tag{6.1}$$

We write the critical scale h_* as a function of the capillary number $\mathrm{Ca} = \mu_0 v/\sigma$ on the basis of Eq. (2.6):

$$h_* = \frac{\varkappa\sigma}{p_*}\,\mathrm{Ca} = \beta\,\mathrm{Ca}. \tag{6.2}$$

The coefficient of surface tension σ does not depend on the D.P. N, so that by virtue of (6.1) the proportionality factor β in Eq. (6.2) does not depend on N. This fundamental fact is appropriately called the theorem of invariance of the scale equation of the viscosity anomaly region $h_* = \beta\,\mathrm{Ca}$ under the D.P. N or the molecular weight of the polymer.

The scale h_* is also conveniently expressed in terms of the macroscopic angle α_0 calculated approximately without regard for the viscosity anomaly according to Eq. (1.7) for the case of statically complete wetting:

$$h_* = \alpha_0^3 H, \quad H = \frac{\sigma}{4\mu_0\dot{\gamma}_* \ln (h_0/h_m)}\,. \tag{6.3}$$

Equations (6.2) and (6.3) can be used to find the limits of validity of the rheological approach, which are deduced from the constraints of the macroscopic description. We first indicate the analogous constraints for the case of a Newtonian fluid.

The method of asymptotic solution of the problem of the dynamic contact angle on the basis of the inequality $\ln(h_0/h_m) \gg 1$, i.e., the existence of a large parameter in the problem, admits [2] the possibility of large errors, of the order of 100%, in the description of the flow near the boundary $h = h_m$; however these errors have asymptotically little influence on the solutions in the region of interest $h \to \infty$. In particular, an e-fold variation of the minimum height h_m of the free surface only slightly affects the solutions $\alpha(h)$ in the limit $h/h_m \to \infty$, because it merely alters the angle α by a small factor of the order of $1/[3\ln(h/h_m)] \ll 1$. We also note that a region having a scale of a few molecular diameters is excluded from the problem in this method, and the flow in it cannot, in principle, be investigated.

These considerations clearly discourage any hope for better than 100% error limits in the macroscopic description for non-Newtonian fluid flow in a region having a scale of a few molecular diameters. Equation (1.7) further corroborates this assessment for the problem with a free boundary.

By virtue of Eq. (6.3), the existence of a minimum scale of the viscosity anomaly region h_* implies the existence of a critical minimum angle $\alpha_{\min}$, at or below which it is impossible to describe the viscosity anomaly region macroscopically:

$$\alpha_{\min} = \alpha_0, \quad h_* = \min h_* = 4a. \tag{6.4}$$

The value $4a$ is adopted here, because the "wedge" in which the flow is analyzed now has a characteristic average thickness of only two molecular diameters, since the average value (scale) of the thickness of the small region is roughly equal to half the minimum thickness, i.e., $0.5h_*$.

According to Eqs. (6.3) and (6.4), the minimum admissible angle is

$$\alpha_{\min} = (4a/H)^{1/3}. \tag{6.5}$$

At the minimum angle $\alpha_0 = \alpha_{\min}$ the rheological approach is not as sensible as the exclusion of a small microscopic region having a scale of two or three molecules from the investigation. And only for sufficiently large angles can the rheological approach be expected to work for closure of the theory in the small-scale case.

The phenomenon whereby rheology of a polymer liquid is manifested only at large dynamic angles α_0 is contrary to the effect of the van der Waals forces, which exert an appreciable influence on the angle α_0 only for extremely small values of the angle ($\alpha_0 \ll 1$) [2]. We have previously arrived at this conclusion [2] on the basis of asymptotic equations that yield good agreement with numerical calculations [11].

The conclusion that the rheological approach is valid only for sufficiently large angles has general implications and is not merely restricted to the specific rheological equation of state.

7. COMPARISON OF THEORY WITH EXPERIMENT

It is instructive to determine the influence of the viscosity anomaly on the theoretical curve of the contact angle as a function of the shear rate for the case of a moving gas–liquid interface in a circular capillary. If rheology is ignored, this curve is known [1, 12] to agree with experiment for polymer liquids [13] and for low-molecular liquids [14].

In the dynamics of complete wetting ($\alpha_m = 0$) of a circular capillary of radius $h_\varkappa$ the contact angle α_0 for a constant viscosity $\mu = \text{const}$ is given by the following equations on the basis of (1.5):

$$\begin{gathered}\alpha_0^3 = \frac{9\mu_0 v}{\sigma} f, \quad \alpha_0 \leqslant 145^\circ, \\ (\pi - \alpha_0)^3 + \frac{9\pi}{4} \ln \frac{1 - \cos\alpha_0}{1 + \cos\alpha_0} = \frac{9\mu_0 v}{\sigma} f, \quad \alpha_0 > 145^\circ, \\ f = \ln(h_0/h_m), \quad h_0 = (1/2)\,\alpha_0^2 h_\kappa, \quad \alpha_0 < 32^\circ; \quad h_0 = 0{,}16 h_\kappa, \quad \alpha_0 > 32^\circ.\end{gathered} \tag{7.1}$$

The value of the constant 0.16 has been found by an approximate calculation [1] for $\alpha_0 \sim \pi/2$.

The coefficient f in (7.1) is given by a different equation in the model with rheology taken into account:

$$f = \Gamma + \ln \frac{h_0}{h_*}, \tag{7.2}$$

where h_* is given by (6.2), and $\Gamma = 2.5$ for $k = 1/2$. We note that the values of Γ and h_* in Eq. (7.2) have the significance of extrapolated values for $\alpha_0 > (3/4)\pi$, since the angles $\alpha(h_*) \sim \pi/2$ are not small in the small viscosity anomaly region.

The molecular diameter a, which is needed in order to calculate h_m, can be estimated from the diameter of a sphere of equivalent volume:

$$a = \left(\frac{6m}{\pi\rho}\right)^{1/3}. \tag{7.3}$$

Here ρ is the density of the liquid, and m is the mass of the molecule. The molecular weight is $M = 1.2 \cdot 10^5$ ($N = 1620$) for the siloxane liquid of viscosity $\mu_0 = 988$ P used in [13] and is $M = 18{,}500$ ($N = 250$) for $\mu_0 = 9.58$ P. Here the characteristic molecular diameters from (7.3) are (respectively)

$$a = 72 \cdot 10^{-8} \text{ cm and } a = 39 \cdot 10^{-8} \text{ cm} \tag{7.4}$$

The characteristic molecular diameter (7.3) is close to the average distance between the centers of gravity of adjacent molecules, which differs from the true molecular diameter in that it does not depend on the degree of mutual entanglement of the polymer molecules.

Estimates of the size of polymer molecules can also be considered on the basis of statistical theory [10]. If free motion of the chain molecule is assumed (ignoring its interaction with adjacent molecules), the mean-square distance between its ends is

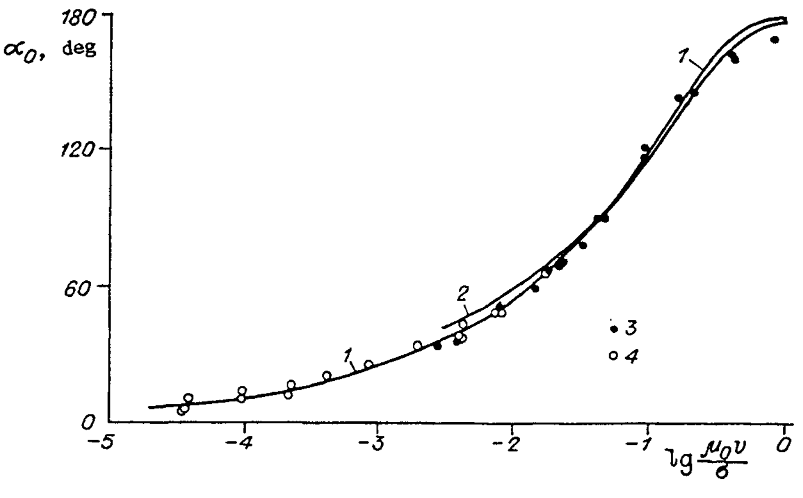

Fig. 5

$$\langle r^2 \rangle = 2c_\infty l^2 N,$$

where the length of the bond is $l = 1.64 \cdot 10^{-8}$ cm, and the constant $c_\infty = 6.43$ in the case of polydimethylsiloxane [10]. If we compare approximately $a^2 \lesssim \langle r^2 \rangle$, we obtain the estimates

$$a \lesssim 90 \cdot 10^{-8} \text{ cm, N} = 250;\ a \lesssim 230 \cdot 10^{-8} \text{ cm, N} = 1620.$$

These estimates are probably high, but do not differ too much from (7.4), at most by a factor of two or three.

If $h_m = 2a$ is determined from (7.4), then $h_m = 0.8 \cdot 10^{-6}$ cm and $1.4 \cdot 10^{-6}$ cm, which imparts a certain stratification to the theoretical curves. However, their stratification is slight, and the average value $h_m = 10^{-6}$ cm [12] is justified for h_m by the fact that a 1.4-fold variation of h_m does not alter the calculated angle α_0 by more than 1%, which does not exceed the admissible computational error limits.

Using the indicated values of the coefficients, we can determine the values of the parameters β and H in the scale equations (6.2) and (6.3) for the viscosity anomaly region, which have the following form for the experiments [13] discussed here with $\mu_0 = 988$ P, $\sigma = 21.7$ dyn/cm, $\gamma_*^{\cdot} \approx 150\ \text{sec}^{-1}$, and $h_\kappa = 10^{-1}$ cm:

$$\beta = 3.3 \cdot 10^{-4} \text{ cm, H} = 3.8 \cdot 10^{-6} \text{ cm.}$$

Taking these values into account, we find the minimum admissible angle from Eq. (6.5) for N = 1620: $\alpha_{\min} = 52°$. In this case it makes sense to calculate the minimum-scale region according to the rheological equations for somewhat larger angles ($\alpha_0 \lesssim 90°$) [4]. If the D.P. N is increased, the minimum admissible angle increases slowly.

In the case of siloxane liquid of relatively low viscosity [$\mu_0 = 9.58$ P (N = 250)] the critical angle is $\alpha_{\min} \sim 35°$, and the rheological approach is therefore effective for $\alpha_0 > 50°$. We note, however, that the model of a power-law dependence of the viscosity on the shear rate works poorly in the case N = 250.

In Fig. 5 the theory applicable to a Newtonian fluid with the closure condition for the minimum scale $h = h_m$ [1] [Eqs. (7.1) (curve 1)] is compared with the rheology-based theory [Eqs. (7.1) and (7.2) (curve 2)] and with experiment [13] (points 3 and 4 for $\mu_0 = 988$ P and 9.58 P, respectively). It is evident from these data that the rheological method of continuous closure for h = 0, where it is applicable, is consistent with the method based on the assumption of a constant viscosity (μ = const). This result corresponds to the analogous conclusion that the results of calculations with allowance for rheology agrees with the results of calculations based on the assumption μ = const in the case of spontaneous spreading of a droplet on a solid surface [1].

It is evident from Fig. 5 that the extrapolation of the rheology-based equations into the range of contact angles comparable with π gives results that exhibit somewhat better agreement with experiment than those according to the theory with μ = const.

In the case of a polymer liquid [13] with the maximum viscosity ($\mu_0 = 988$ P) the large value of the minimum contact angle at the boundary ($\alpha_{min} = 52°$) and the justification of the rheological approach for even larger angles ($\alpha_0 \gtrsim 90°$) rule out the theoretical description of a significant portion of the experimental points from [13] by the rheological approach. In the case of a polymer liquid [13] with $\mu_0 = 9.58$ P a large part of the experimental data remains outside the region of validity of the method of closure of the theory with allowance for rheology on the basis of the condition imposed directly on the solid surface at $h = 0$.

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