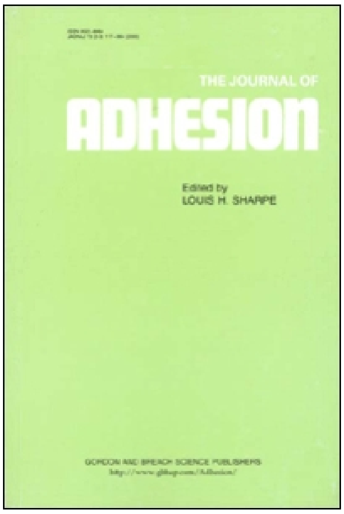

The Journal of Adhesion
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Rheology of Sintering, Spreading and Leveling of Fluids

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To cite this Article Vanoene, H.(1972) 'Rheology of Sintering, Spreading and Leveling of Fluids', The Journal of Adhesion, 4: 3, 247 — 259
To link to this Article: DOI: 10.1080/00218467208072227
URL: http://dx.doi.org/10.1080/00218467208072227

J. Adhesion, 1972, Vol. 4, pp. 247-259

Printed in Northern Ireland

Rheology of Sintering, Spreading and Leveling of Fluids†

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(*Received February* 3, 1972)

Hydrodynamic aspects of free surface flows are discussed within the framework of Orchard's theory of leveling in order to assess the validity of theories based on a thermodynamic analysis such as Frenkel's theory of sintering. Principal conclusions are that (i) there is hydrodynamic justification for the viscous dissipation function assumed by Frenkel; (ii) in spreading one needs to take into account a possible hydrodynamic retardation, (iii) terminal spreading rates can be accounted for by the theory of Smith, which considers only gravitational forces; (iv) further useful extensions of the hydrodynamic theory allow for analysis of the influence of viscoelasticity and heterogeneity of the fluid on such free surface flows.

INTRODUCTION

The flow during sintering, spreading and leveling of fluids will be discussed within their common hydrodynamic framework of free surface flows. These flows are characterized by the fact that the surface tension forces, which define a surface state of stress, induce a change of shape of the material. It is useful to treat these flows jointly since in practice one observes frequently the combined effects of sintering, spreading and leveling as for instance in powder-coating, a process whereby a powder is applied to a substrate; on heating the powder melts, covers the substrate by spreading and sintering, the resulting uneven liquid film levels, leaving a more or less smooth adherent film on cooling.

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† This paper was presented at the *Symposium on Recent Advances in Adhesion* during the 162nd National American Chemical Society Meeting, September, 1971.

Two aspects of these flows are of particular interest:

(i) what is the rate of each individual flow
(ii) what are the bulk motions of the material during these flows.

The rate of flow is usually obtained from a measurement of the change of shape of the material. This is therefore determined by the motion of the bounding surface itself. The bulk motions are determined by the streamlines and will provide information about the material transport. It turns out, that theoretically in many circumstances the surface velocities are more easily obtained than the bulk streamlines. The latter aspect is, however, of considerable importance when the fluid itself is heterogeneous.

In the literature two distinct approaches have been used to treat these free surface flows in a quantitative fashion:

I. A thermodynamic approach[1,2,3]

A representative example of which is Frenkel's theory of sintering[1]. In this theory the work required for a change in shape of the material is calculated from the decrease in surface free energy. This work is dissipated by viscous flow. The magnitude of the energy dissipation must, however, be calculated from an assumed shear field. The quantitative predictions of these theories depend therefore on the correctness of this choice.

II. A hydrodynamic approach[4]

In these theories the decrease in surface free energy is ignored. Instead, one chooses a particular simple free surface flow: the flow of a liquid film over a horizontal or inclined substrate. The stability of this flow to a disturbance of the free surface, which may take the form of a surface corrugation, may now be studied. The damping of the surface corrugation can be taken as a measure of the rate of leveling. This simple hydrodynamic model has proven itself to be a very powerful tool for the detailed analysis of the effect of a change in surface properties such as surface elasticity, surface viscosity, surface tension gradients, imposed gradients of mass transfer and temperature[5] and bulk viscoelasticity[6] on the damping or amplification of the surface corrugation.

In this article the known hydrodynamic solutions will be analyzed further in order to clarify the hydrodynamic assumptions made in thermodynamic type theories. In the light of this analysis, good agreement between recent experimental investigations of sintering and drop spreading and theory can be achieved. Secondly, the hydrodynamic discussion will be extended in order to explore the extent of bulk flow when a layer of finite thickness, which differs in viscosity and surface tension, from the bulk, covers the original corrugated liquid film.

THEORY

I. Thermodynamic approach

The model first proposed by Frenkel[1] will be used. Following Manson and co-workers[7], however, no geometrical approximations will be made other than those inherent in the Frenkel model, which treats the neck region as two interpenetrating spheres. The model is illustrated in Figure 1. The results may be summarized as follows:

FRENKEL MODEL

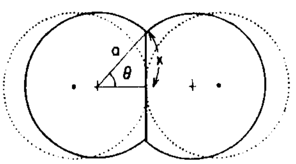

FIGURE 1 Frenkel model, to scale. The distance between the center dot and cross represents the required amount of shrinkage.

(i) the constant total volume condition, provides an expression for the current radius a of the spheres:

$$a = a_0 4^{1/3}(2 - u)^{-2/3}(1 + u)^{-1/3} \tag{1}$$

where $u = 1 - \cos\theta$ and a_0 is the initial radius of the sphere.

(ii) the work per unit time done by the surface tension forces is given by:

$$\gamma\frac{d\Delta S}{dt} = \gamma\frac{d\Delta S}{du}\frac{du}{dt} = 4\pi a_0^2\gamma 4^{2/3}(1 - u)(1 + u)^{-5/3}(2 - u)^{-4/3}\frac{du}{dt} \tag{2}$$

where ΔS is the decrease in surface area, and γ the surface tension.

(iii) the viscous energy dissipation is calculated from the rate of change of the extent of flow, reduced by the value of the current radius. The "velocity-gradient" q is therefore:

$$q = \frac{1}{a}\frac{dau}{dt} = (2 - u)^{-1}(1 + u)^{-1}(2 + u)\frac{du}{dt} \tag{3}$$

and the energy dissipation:

$$2\cdot\frac{8\pi}{3}a_0^3\eta(2 - u)^{-2}(1 + u)^{-2}(2 + u)^2\left(\frac{du}{dt}\right)^2 \tag{4}$$

(iv) equating the work/unit time done by the surface tension forces and the viscous energy dissipation yields:

$$\frac{du}{dt} = \tfrac{3}{4}(\gamma/a_0\eta)4^{2/3}(1 - u)(1 + u)^{1/3}(2 - u)^{2/3}(2 + u)^{-2} \tag{5}$$

which expression may be integrated numerically. Manson and Nippert[7] simplify Eq. 5 somewhat by noting that $(2 + u)^2 = 4(1 + \tfrac{1}{2}u)^2 = 4(1 + u + \tfrac{1}{4}u^2)$, neglecting $\tfrac{1}{4}u^2$ inside this bracket gives:

$$\frac{du}{dt} = \tfrac{3}{4}(\gamma/a_0\eta)(1 - u)[(2 - u)/2(1 + u)]^{2/3} \tag{6}$$

for small θ, $u = 1 - \cos\theta \approx \tfrac{1}{2}\theta^2$ hence:

$$\theta^2 = \tfrac{3}{2}(\gamma/a_0\eta)t \tag{7}$$

which is the original Frenkel equation. As implicit in Frenkel's paper and emphasized by Manson and co-workers, Eq. 7 is valid only for $\theta < 30°$. Since most experimental data fall outside this range a valid experimental comparison can only be made with the integrated expression. Strella[3] proposed recently a slightly different set of equations. He uses a different choice of "velocity-gradient" (the reduced rate of change of the total distance to the interface) and takes the energy dissipation to be given by

$$3V\eta\left\{(1 + u)^{-1}\frac{du}{dt}\right\}^2,$$

where V is the volume of the droplet. When the factor 3 is replaced by the more hydrodynamically motivated factor of 2, Strella's expression for the sintering rate becomes:

$$\left(\frac{du}{dt}\right) = \tfrac{3}{4}(\gamma/\eta a_0)4^{2/3}\frac{(1 - u)}{(2 - u)}\left(\frac{1 - u}{2 - u}\right)^{1/3} \tag{8}$$

When the factor of three is retained, the front factor $\tfrac{3}{4}$ should be replaced by $\tfrac{1}{2}$. From the assumptions made by Strella, it appears that his formula may be more applicable to the sintering of one sphere to a flat plate than the sintering of two spheres. It is seen that the relative success of this approach lies in the fact that:

(i) the change in surface area may be calculated without approximation
(ii) the work done by the surface forces may be related to a surface velocity
(iii) the viscous energy dissipation is proportional to the square of the surface velocity.

This last point, however, needs hydrodynamic justification.

II. Hydrodynamic theory

For the present purposes, it is sufficient to restrict the analysis to the surface leveling of a viscous, horizontal film, of finite thickness but infinite in extent in the other directions. The problem reduces therefore to two dimensions, which simplifies the subsequent analysis immensely. As stated in this form, Orchard's[8] solution is directly applicable. The problem itself, however, has a long history in the guise of the stability analysis of free surface flows and in connection with waves on liquids[4,9].

Since the analysis may be carried out in two dimensions, the hydrodynamic equations reduce to the problem of finding a stream function. The boundary conditions are:

(i) at the free surface the velocity gradient vanishes
(ii) at the fixed surface the velocities vanish.

When the free surface's elevation, around the *mean* surface $y = 0$, is expressed in terms of a complex Fourier series:

$$S(x) = i \sum_{n=-\infty}^{n=+\infty} a_n \exp(ik_n x) \tag{9}$$

where k_n is the wave number $2\pi/\lambda_n$; the stream function expressed as:

$$\phi = \sum_{n-\infty}^{n+\infty} \exp(ik_n x)\, F_n(y) \tag{10}$$

which implies that the velocities are given by: $u = \partial\phi/\partial y$ and $v = -\partial\phi/\partial x$, the following differential equation results:

$$\left[k_n^4 - 2k_n^2 \frac{d^2}{dy^2} + \frac{d^4}{dy^4}\right] F_n(y) = 0 \tag{11}$$

This differential equation is central to the stability analysis. Omitting further details, it is found that for a particular Fourier component k_n the stream-function is given by:

$$\phi = e^{ikx}(A \cosh(ky) + B \sinh(ky) + Cy \cosh(ky) + Dy \sinh(ky)) \tag{12}$$

where the constants are

$$B = \gamma a/2\eta, \quad A = Bf(\theta), \quad C = -kBg(\theta) \quad \text{and} \quad D = -Bkf(\theta) \tag{13}$$

and

$$f(\theta) = [(\tanh\theta - \theta \operatorname{sech}^2\theta)/(1 + \theta^2 \operatorname{sech}^2\theta)] \tag{14}$$

$$g(\theta) = 1/(1 + \theta^2 \operatorname{sech}^2\theta) \tag{15}$$

the parameter $\theta = kh$, with h the thickness of the film; a is the amplitude of the disturbance, γ the surface tension and η the viscosity. When the free surface is represented by the real function $y = -a \sin kx$, the velocities are:

$$u = Bk \cos kx[(1 - g(\theta)) \cosh (ky) - f(\theta)ky \cosh (ky) - g(\theta)ky \sinh (ky)] \tag{16a}$$

$$v = Bk \sin kx[\sinh ky + f(\theta) \cosh ky - f(\theta)ky \sinh ky - g(\theta)ky \cosh (ky)] \tag{16b}$$

For the case $h = \lambda$, $\theta = 2\pi$, these velocities are plotted in Figure 2, 3. These velocities are interesting in themselves. At the crest of the corrugation the velocities are downwards, at the trough of the corrugation upwards, nevertheless no "cells" exist. It is also seen that most of the bulk motion is confined to a surface layer about $\frac{1}{4}$ wavelength thick. The rate of leveling can be obtained from the surface velocities directly, or by calculating the mean flow through the nodal planes at $kx = 0$ and $\pi/2$. Either way one finds:

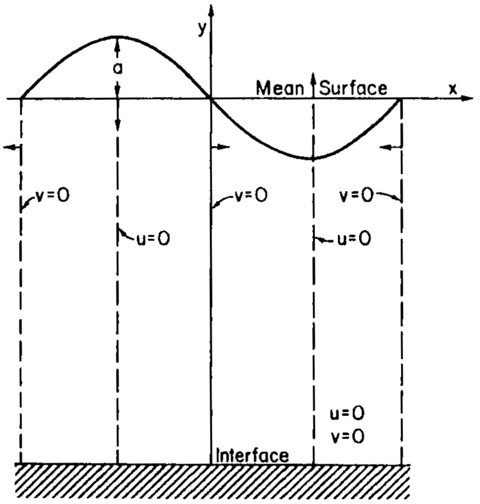

FIGURE 2 Orchard model, schematic. The arrows indicate the directions of the bulk flow.

$$\frac{da}{dt} = -Bkf(\theta) = -(B/h)\theta f(\theta) \tag{17}$$

or

$$a = a_0 \exp [-\tfrac{1}{2}(\gamma/\eta h)\theta f(\theta)]t \tag{18}$$

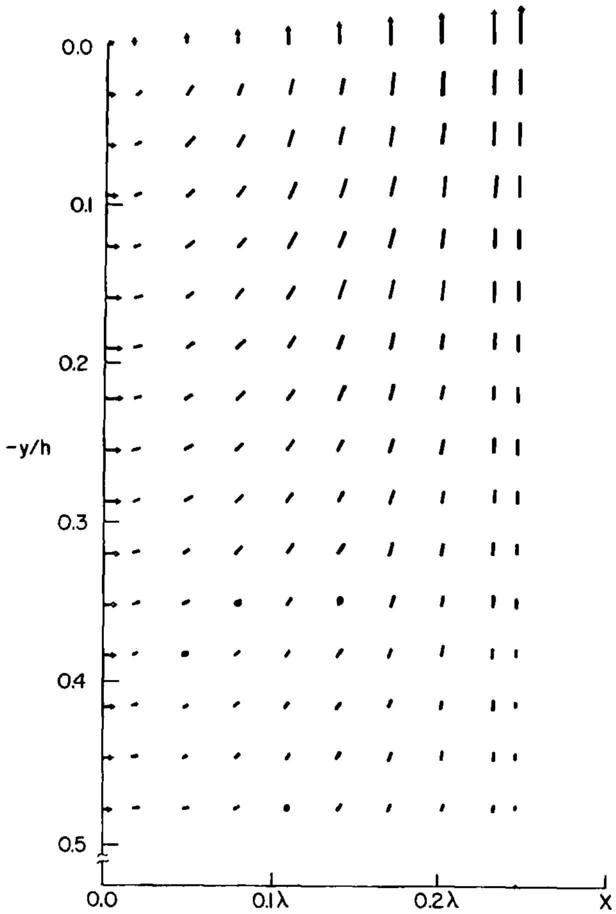

FIGURE 3 Velocities calculated from the Orchard model. The length of the arrows is proportional to the magnitude of the velocity.

where a_0 is the initial value of the amplitude. The energy dissipation, due to viscous flow is given by[10]:

$$2F = \frac{1}{k^2}\int_{-\theta}^{0}\int_{0}^{\pi}\Phi\, d(kx)\, d(ky) \tag{19a}$$

where

$$\Phi = \eta\left[\left(\frac{dv}{dx} + \frac{du}{dy}\right)^2 - 4\frac{du}{dx}\frac{dv}{dy}\right] \tag{19b}$$

Integration yields:

$$2F = \tfrac{1}{2}\pi B^2k^2\eta[2f(\theta) + \{2 - 2g(\theta) + (2\theta^2 + 1)(g^2(\theta) + f^2(\theta)) + 4\theta f(\theta)\}\sinh 2\theta$$

$$- \{2f(\theta) + 2\theta f^2(\theta) + 4\theta g(\theta) - 2\theta g^2(\theta) + 4\theta^2 f(\theta)g(\theta)\}\cosh 2\theta] \quad (20)$$

When $\theta \geq 2\pi g(\theta) = f(\theta) = 1$, the integral reduces considerably, and:

$$2F = \pi B^2k^2\eta[1 - e^{-2\theta}\{2\theta^2 + 2\theta + 1\}] \quad (21)$$

for sufficiently large θ; therefore, one obtains:

$$2F \approx \pi B^2k^2\eta \quad (22)$$

hence

$$2F = \pi\eta\left(\frac{da}{dt}\right)^2 \quad (23)$$

In this limit the energy dissipation is indeed proportional to the square of the surface velocity. In the limit of small θ, i.e. large wavelengths one obtains:

$$2F \approx \tfrac{2}{3}\pi B^2k^2\theta^3 \approx \pi B^2k^2\eta f(\theta) \quad (24)$$

hence for $\theta \to 0$

$$2F \approx \pi\eta\left(\frac{da}{dt}\right)^2 1/f(\theta) \quad (25)$$

In general the energy dissipation is not proportional to the square of the surface velocity or rate of leveling. For $\lambda \leq h$ an equation of this type, however, is obtained.

DISCUSSION

The hydrodynamic characteristics of free surface flows may be readily deduced from Orchard's theory. When $\theta \gg 2\pi$, i.e. $\lambda \leq h$ the surface velocity is only dependent on the wavelength of the disturbance, but independent of film thickness. In addition, the viscous dissipation is proportional to the square of the leveling velocity. Since the rate of decrease of arc length—which replaces surface area in a two-dimensional theory—is proportional to da/dt one could construct a Frenkel type theory for the magnitude of da/dt.

Since sintering involves the motion of a free surface only, a Frenkel type theory may indeed be justified for this flow. Such a theory, however, should not be applicable to spreading over a substrate. Due to the presence of a fixed boundary, the thickness/wavelength ratio θ is increasingly important as the wavelength of the disturbance becomes larger than the thickness of the film. As will be justified subsequently, one may take θ in drop spreading to be given by the expression: $\theta = 2\pi(\frac{1}{2}h/4R) = (\pi/4)(1 - \cos\phi)$, where ϕ is the contact angle. Hence for $\phi \leq 90°$, $\theta < 2\pi$, which indicates that the solid substrate retards the motion.

Regardless of the detailed boundary conditions, the hydrodynamic theory leads directly to the commonly observed fact of superposition with respect to the ratio γ/η.

The theoretical discussion may be summarized as follows: Free surface flows are characterized by relationships of the type:

$$\text{surface velocity} \propto \gamma/\eta L f(\theta)$$

where L is a scaling length, the wavelength of the disturbance, and $f(\theta)$ a function determined by the hydrodynamic boundary conditions, independent of γ/η.

Comparison with experimental results

Sintering. In Figure 4 the data of Manson and co-workers[7] are plotted in reduced form. The drawn line represents the theoretical results obtained by numerical integration of equation 6. The shift factors obey the WLF equation for polymethylmethacrylate, hence confirming superposition with respect to viscosity. The quantitative comparison of initial slopes and those calculated by means of equation 7, reveals agreement to within a factor of two. This may reflect either experimental error or a deficiency in theory. The possible influence of viscoelasticity will be discussed separately.

Drop Spreading. Our earlier work[11] revealed already good qualitative agreement with the hydrodynamic features of the flow of liquid films, provided the "equivalent" thickness of the film was not specified. The equivalent thickness was found to depend on the time dependent contact angle ϕ. The initial spreading rate dr/dt turned out to be given by:

$$\frac{1}{R_0}(dr/dt)_{t\to 0} = \frac{1}{R_0}(dh/dt)_{t\to 0} = 0.063\ \gamma/\eta R_0 \cdot \cos\phi_\infty\ . \tag{26}$$

The theory of Orchard does not deal with the spreading rate, but the decrease in height, which according to Eq. 18 is given by:

$$\ln h/R_0 = -\tfrac{1}{2}(\gamma/\eta h)\theta f(\theta) \cdot t \tag{27}$$

In the drop spreading experiment the Orchard parameter θ decreases with time, but it also implies that, regardless of the particular value of θ, the decrease for each particular value of θ is still exponential with time. Hence for each point a value of the function $\theta f(\theta)$ may be calculated. An experimental check on the theory is then possible provided θ can be calculated independently. Some caution is, however, in order, since the hydrodynamic

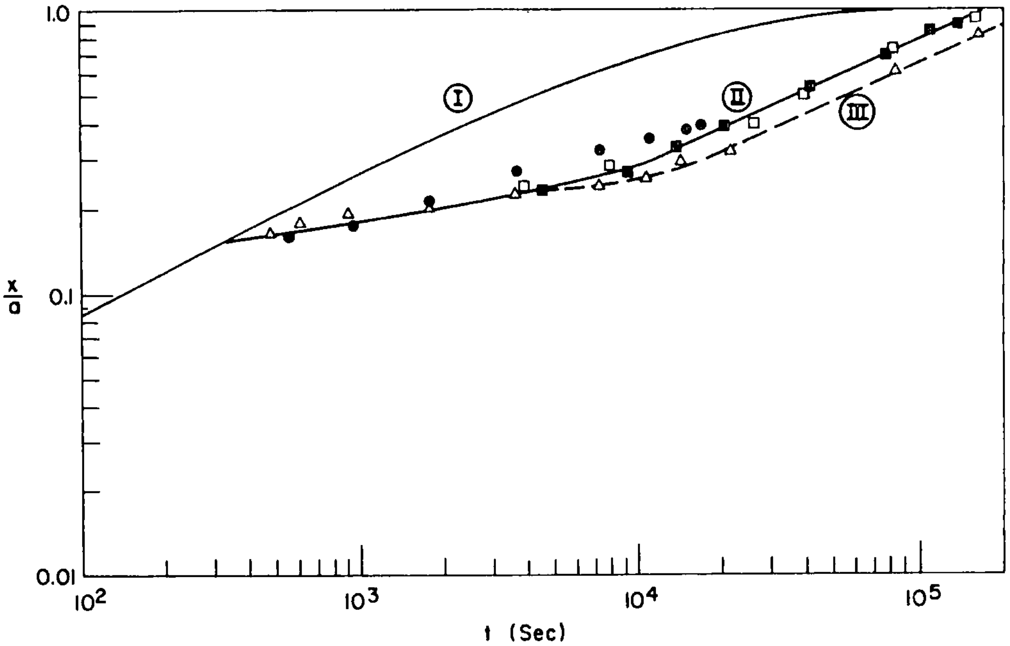

FIGURE 4 Sintering curve for Lucite 40, reduced to $T = 148$ (Ref. 7).

Legend:

- ■ $T = 200°$ C
- □ $T = 178°$ C
- ● $T = 168°$ C
- △ $T = 148°$ C

Curve I *a priori* Frenkel prediction for $T = 148$, obtained by integration of equation 8.
II reduced curve described by the high temperature data
III experimental curve obtained at $T = 148$

The displacement of curve II and III may be a visco-elastic effect.

treatment is only a two-dimensional theory, hence exact quantitative agreement cannot be expected. It turns out, that initially quantitative agreement can be obtained if the ratio $(\gamma/\eta h)$ is taken to be given by $\gamma/\eta R_0$, hence:

$$\ln h/R_0 = -\tfrac{1}{2}(\gamma/\eta R_0)\theta f(\theta)t \tag{28}$$

with:

$$\theta = \frac{\pi}{4}(1 - \cos\phi)$$

In this form the equations may be directly compared with experimental data. The data in reference 11 were all reduced to the experimental data for the sample DYLT at 120°C. Only the data for this sample will therefore be used. It is found that for: $t = 180$ sec., $\gamma/\eta R_0 = 5.36 \times 10^{-2}$, $\phi = 72°$, $h/R = 0.843$, $(1 - \cos \phi) = 0.691$.

The function $\theta f(\theta)$ as calculated from equation 28 is equal to 0.035. From Table I this implies a value of θ equal to 0.53. The independently calculated value of θ is equal to 0.54. The parameters have therefore been chosen in a consistent fashion. When $\phi \rightarrow 90°$, $t \rightarrow 0$, $\theta \rightarrow \pi/4$, hence $\theta f(\theta) = 0.12$ (Table I). The proportionality factor for the initial rate is therefore 0.06, again in good agreement with the experimentally observed value 0.063. At intermediate angles, say $\phi \approx 45$, the experimentally determined θ is about twice the value calculated directly. At long times these equations predict velocities of the order of 10^{-5}–10^{-6} cm/sec, which are distinctly too small. The influence of gravity has however been ignored. This influence can, fortunately, be calculated exactly by means of a recent analysis of Smith[12] who treated the rate of spreading of a viscous sheet of liquid confined, initially, at the origin of the coordinate system. The rate of spreading is found to be given by:

TABLE I

Values of θ and $\theta f(\theta)$

θ	$\theta f(\theta)$	θ	$\theta f\theta$	θ	$\theta f\theta$
.80	.1277	.60	.0526	.40	.0133
.79	.1231	.59	.0498	.39	.0121
.78	.1185	.58	.0471	.38	.0110
.77	.1140	.57	.0445	.37	.0100
.76	.1097	.56	.0420	.36	.908 E-2
.75	.1054	.55	.0396	.35	.820 E-2
.74	.1012	.54	.0372	.34	.738 E-2
.73	.0971	.53	.0350	.33	.661 E-2
.72	.0931	.52	.0328	.32	.590 E-2
.71	.0892	.51	.0308	.31	.525 E-2
.70	.0854	.50	.0287	.30	.465 E-2
.69	.0817	.49	.0269	.29	.410 E-2
.68	.0781	.48	.0250	.28	.359 E-2
.67	.0746	.47	.0233	.27	.313 E-2
.66	.0712	.46	.0216	.26	.272 E-2
.65	.0679	.45	.0201	.25	.234 E-2
.64	.0646	.44	.0185	.24	.200 E-2
.63	.0615	.43	.0171	.23	.170 E-2
.62	.0584	.42	.0158	.22	.144 E-2
.61	.0555	.41	.0148	.21	.120 E-2
				.20	.995 E-3
				.10	.655 E-4

$$d(r/R_0)/dt = 0.13(gR_0/v)^{1/8}t^{-7/8} \tag{29}$$

where r is the spreading distance; g, the acceleration due to gravity; R_0, the initial radius of the drop and v, the kinematic viscosity. At long times the experimentally observed spreading data may be fitted by an expression of the form[13]:

$$\frac{1}{\cos \phi} = 1 + \frac{1}{kt} \tag{30}$$

which for large kt leads to:

$$d(r/R_0)/dt = 0.206k^{1/6}t^{-5/6} \tag{31}$$

The experimental exponent 0.83 is close to the theoretically predicted value of 0.87, the more so since the experimental value is implied by the form of the function chosen to represent the time dependence of $\cos \phi$. The absolute values of the velocities may now be calculated and compared. The results are: (for the sample DYLT and t 10^4 sec.)

T	120	140	160
velocity ($\times$ 10^4) eqn. 29	0.25	0.28	0.30
velocity ($\times$ 10^4) eqn. 31	0.19	0.34	0.36

The velocities calculated from Orchard's expression would be of the order of 10^{-7} cm/sec. The effect of gravity may therefore certainly not be neglected.

In summary, the kinetics of sintering and spreading of homogeneous liquids can be adequately described within the framework of the theories outlined. Hence more complex phenomena such as observed during free surfaces flows of heterogeneous fluids (mixtures) can be analyzed. Experimentally one observes a considerable amount of phase separation, caused by the sintering and spreading processes. Since such phenomena involve the motion of the bulk as well as the motions at the free surface, the preceding analysis indicates that the simple Orchard model may be a satisfactory starting point for further analysis. More detailed results will be presented at the meeting.

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Acknowledgement

Professor J. A. Manson, Materials Research Center, Lehigh University, Bethlehem, Penn., kindly supplied the results of the numerical integration and the values of the physical paramerers of Lucite 40.