Spreading of a non-Newtonian liquid drop over a horizontal plane

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ABSTRACT

The spreading of a drop of non-Newtonian (power-law) liquid over a horizontal solid substrate is analyzed theoretically through energy approach method in the case of complete wetting. In this approach we have used the physical and geometrical reasoning and finally obtained a relation between the rate of spreading and bottom radius of the drop. It is shown that spreading rate of shear thickening liquid is more than that of a Newtonian liquid while shear thinning liquid is having slower rate than the latter one.

1. Introduction

Fundamental understanding of the spreading mechanism is important to gain control over several industrial applications. In general, the spreading process of liquid drop on any substrate is too complex phenomena. Since, this process depends on many factors like viscosity, surface tension, density, volatility, solid surface roughness, texture, chemical heterogeneity, drop size, even on rheological parameters if the liquid is non-Newtonian etc. Such type of motion may be defined mathematically through non-linear differential equation with so many conditions.

Spreading of liquid over solid surface has been studied extensively from both theoretical and experimental points of view by several researchers viz. Marmur (1983), Cazabat (1987), Léger and Silberzan (1990), Ehrhard (1993), Seaver and Berg (1994), Bahr et al. (1999) and many others. Mainly, the spreading process can be divided into two categories i.e. high speed impact spreading and low-speed spreading. In fact, former one is called the inertia dominated or forced spreading and the latter one is called surface tension dominated spreading. The spontaneous spreading occurs when the impact speed is equal to zero. The forced spreading of liquid drop is widely encountered in case of spray coating and it is shown that the final shape of the drop depends on impinging speed only, when the impinging speed is

greater than some critical value and this critical value varies from liquid to liquid. In last two decades lot of theoretical and experimental models on spreading process of a drop have been reported in the literature. Most of these models are related to the spreading of Newtonian liquid on a solid or porous substrate. For Newtonian liquid, Tanner (1979) first gave an empirical relation between the rate of spreading over a solid surface with the bottom radius of the drop. Mainly in the process of spreading, one may think of the total energy of the drop may be divided into two parts, namely the energy associated with the volume and the energy associated with surfaces. For a large drop spreading over an impermeable surface, the gravitational potential energy is converted into the kinetic energy of the liquid flow. But when the drop size is too small (sub-millimeter level), the surface energy dominates the spreading process. The volume-associated energy for a spherical droplet of volume V, radius R, mass m and density ρ can be represented by its potential energy and this energy is converted to kinetic energy during flow. Therefore, we have

$$E_v = mgR = \rho VgR = \frac{4\pi}{3} R^4 \rho g. \tag{1}$$

The surface-associated energy can be estimated as

$$E_s = 4\pi R^2 \sigma, \tag{2}$$

where σ is the surface tension of the liquid. Both the energies will be at par when

$$R_{capillary} = \sqrt{\frac{3\sigma}{\rho g}}. \tag{3}$$

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This $R_{capillary}$ is known as the *capillary length*, see de Gennes (1985). For a typical silicone oil (TSIL - 080) with $\sigma = 21 \times 10^{-3}$ J/m^2 and $\rho = 970$ kg/m^3, we have $R_{capillary} \sim 2.6$ mm. If the droplet size is much smaller than the $R_{capillary}$ then the motion is due to the conversion of the surface energy. de Ruijter et al. (1999), Aradian et al. (2000), Gu and Li (1998, 2000), Erickson et al. (2001), Daniel and Berg (2006) and Attané et al. (2007), have applied energy based model to analyze the different physical aspects of the drop spreading phenomena. Spreading of a drop of non-Newtonian liquid has also several industrial applications like ink-jet printing and spray coating, etc. So the attention of several researchers (Biswas and Gupta, 1987; Starov et al., 2003; Rafai and Bonn, 2005; Wang et al., 2007a, 2007b and others) have been drawn to study the non-Newtonian effects. It is interesting to note that, so far, to the best of our knowledge, none has considered the energy approach to study the spreading of a non-Newtonian liquid drop. In this study, our interest is to analyze the spreading process based on energy approach only.

2. Theoretical model of spreading

Let us consider a liquid drop placed on a flat solid surface with vapour/liquid, liquid/solid and vapour/solid interfaces that con-join at a contact line. The solid is assumed to be chemically homogenous, smooth and not to be dissolved or react with the liquid.

Equilibrium shape of a drop is determined by the action of the interfacial properties of solid, liquid and surrounding gas or vapor. In other words, the interfacial energy that stored within the drop starts to dissipate in course of time as a result the drop spreads on the surface. In this analysis, we have assumed that the volume of the drop remains constant and its shape is a spherical cap so that its surface free energy is minimized or in other words the drop attains its lowest energy configuration. A typical shape of a drop and its surroundings is represented in Fig. 1.

Helmholtz surface free energy of the drop becomes

$$F^S = \sigma_{LG}A_{LG} + \sigma_{SL}A_{SL} + \sigma_{SG}A_{SG}, \tag{4}$$

where A_{LG}, A_{SL} and A_{SG} represent the liquid–gas, solid–liquid and solid–gas interfacial areas, respectively. σ_{LG}, σ_{SL} and σ_{SG} denote surface tensions of A_{LG}, A_{SL} and A_{SG}, respectively. Further it is to be remembered here that the change of the free energy takes place due to geometric shape change of the droplet keeping total volume fixed. There are number of paths of the evolving process through which free energy can reduce. Our consideration of the spherical cap drop shape with its bottom radius a and height h give

$$F^S = \pi(a^2 + h^2)\sigma_{LG} + \pi a^2 \sigma_{SL} + (A_{tot} - \pi a^2)\sigma_{SG}, \tag{5}$$

where $A_{tot}(=A_{SL}+A_{SG})$ is the total area of the solid substrate. Here, surface free energy is expressed in terms of interfacial energies and two geometrical parameters i.e. a, h. Since, in case of pure spreading (i.e. spreading on non-porous smooth solid sub-strates), volume V remains constant and let its initial volume V_0 (Tadmor, 2004) with height h depends upon the drop radius a as

$$V_0 = \frac{\pi}{6}h(3a^2 + h^2). \tag{6}$$

Constant volume during spreading process demands

$$\frac{dh}{da} = -\frac{2ah}{a^2 + h^2}. \tag{7}$$

Differentiating Eq. (5) with respect to a and using the value of dh/da from (7), we get

$$\frac{dF^S}{da} = 2\pi a\left[\cos\theta - \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}}\right]\sigma_{LG}, \tag{8}$$

where θ is the dynamic contact angle (see Fig. 2). Minimization of the surface free energy (F^S) requires

$$\cos\theta = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}}, \tag{9}$$

provided real θ exists. Existence of θ is defined as the equilibrium contact angle (θ_{eq}^V) and we have

$$\cos\theta_{eq}^V = \frac{\sigma_{SG} - \sigma_{SL}}{\sigma_{LG}}. \tag{10}$$

The surface free energy expression is important because it explains about the driving force for the spreading process, which is often easier to determine with respect to hydrodynamic approach. From the above analysis it is not possible to understand how fast the spreading process takes place until and unless we relate the geometric change of the liquid/vapour interface and contact line with the thermodynamic forces acting on them. Assuming the whole process is isothermal and reversible we have the total Helmholtz free energy (F) in terms of dissipative process as

$$\frac{dF}{dt} = -\Sigma \int_{V_i} \mu\phi_i dV_i. \tag{11}$$

Here, $\mu\phi_i$ is the local viscous dissipation occurring in a volume element dV_i in the 'i'th region of the system. The right hand side of the above equation represents the sum of viscous dissipation terms. For a single drop, we have

$$\frac{dF^S}{dt} = -\int_V \mu\phi_{drop} dV, \tag{12}$$

where V is the volume of the drop. It is to be noted here that our present system is incompressible and the exchange of liquid from the drop is prohibited, the only modes of free energy change are related with the surface. In this case, the free energy change is equivalent to expression (8). Thus,

$$2\pi a[\cos\theta_{eq}^V - \cos\theta]\sigma_{LG}\frac{da}{dt} = \int_V \mu\phi dV, \tag{13}$$

and is equivalent to the viscous energy equation introduced by de Gennes (1985). We are now interested to calculate the energy
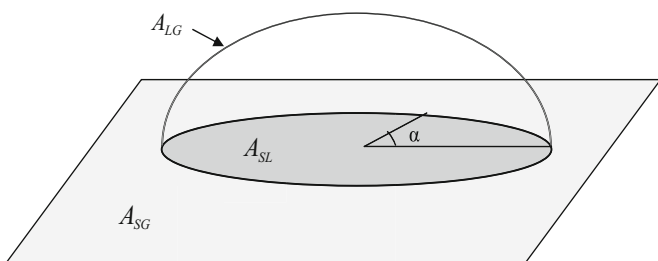

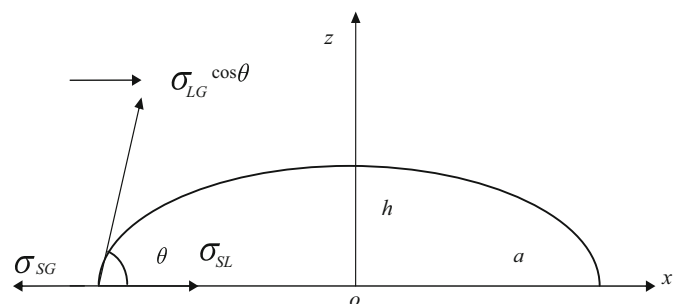**Fig. 1.** Representation of drop surfaces.

Fig. 2. Representation of balance of interfacial forces in *x*-direction.