

# FLUID MECHANICS

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## Transient Motion of a Drop in Boundless Liquid with Surfactants

### 1. Introduction

Let a viscous drop being in an ambient viscous liquid with diluted surfactants begin to move under the action of gravity force  $g(t)$  depending on time  $t$ . Due to the dilatation of fluid-fluid interface  $\Gamma$  bounding the drop, the thermodynamic equilibrium is disturbed and an additional reactive capillary force arises, which decelerates the drop motion [16]. In other words the well-known Le Chatelier's principle is valid here. This conclusion is based on the fundamental thermodynamic laws whose successive application leads to the symmetrical form of heat and mass transfer equations provided that they are written in intensive thermodynamic variables [2, 3].

The motion of viscous drops driven by buoyancy and capillary forces in an ambient flow field, have been the subject of a number of studies (see, e. g. [1, 2, 5, 7, 12, 13, 14, 16, 21-23]). Most of the studies have concentrated on the interaction between the drop and the ambient flow, with a view to predicting the drop's speed and deformation. The present paper is devoted to the further development of the approach given in [2] where the symmetrical form of capillary fluid mechanics equations has been first obtained for a special case, and the influence of variable surface tension on the transient motion of a drop has been calculated.

The principal idea of symmetrization of gas dynamics equations has been enunciated by Godunov [9]. His approach has been further expanded for magnetohydrodynamics [10], theory of elasticity [11], and effectively exploited for solving the stability problems for shock waves, and for the finite difference scheme design. The general mode of symmetrization of interface dynamics equations, including phase transitions equations, is given in [2-4].

### 2. Thermodynamics of interface

From mechanical point of view, the capillary forces have an internal nature, and their determination is a problem of the multiphase liquid rheology. The principal difference of capillary fluids and the Newtonian ones is connected with the anisotropy of

stresses in the contact layers of liquid phases, i. e., the Pascal's law is not true here. In actual practice, the interphase region has very small thickness being constant during processes of fluid flows. Consequently, the interphase layer could be approximated by the Gibbs' dividing surface  $\Gamma$ , supplied by distributed abundant extensive thermodynamic variables such as surface internal energy  $\varepsilon$ , concentration  $\gamma$  of surfactants, and entropy  $\eta$  [8]. Of course, the temperature  $\theta$  and the chemical potential  $\zeta$  of surfactant, which are intensive thermodynamic variables, must be continuous everywhere including  $\Gamma$ . Interface  $\Gamma$  is identified with an open thermodynamic system being in contact with bulk phases which play a role of a reservoir of heat and surfactant molecules. The briefly-described Gibbs' approach allows us to eliminate the rather complex subject of structure and thickness of the interphase layer, and to apply effective methods of thermodynamics to capillary phenomena.

To remind the definition of the surface tension, let us consider a closed thermodynamic system of two liquids separated by a homogeneous interface  $\Gamma$  of area  $A$ . Let  $E$  be the total internal energy,  $N$  be the total number of surfactant molecules,  $S(E, N)$  be the entropy of the bulk phases, and  $A\eta(\varepsilon, \gamma)$  be the abundant entropy of surface  $\Gamma$  (the given dependence  $\eta(\varepsilon, \gamma)$  determines completely the interface thermodynamics). The entropy maximum principle

$$S(E - A\varepsilon, N - A\gamma) + A\eta(\varepsilon, \gamma) \rightarrow \max,$$

under conditions  $A\varepsilon \ll E$ ,  $A\gamma \ll N$  (the reservoir is much more larger than the open system  $\Gamma$ ), leads to the variational problem

$$\eta(\varepsilon, \gamma) - \varepsilon/\theta + \gamma\zeta/\theta \rightarrow \max,$$

where the well-known equalities

$$\frac{1}{\theta} = \frac{\partial S(E, N)}{\partial E}, \quad \frac{\zeta}{\theta} = -\frac{\partial S(E, N)}{\partial N}$$

for the bulk phases were taken into consideration [17].

Under some mild assumptions, such as concavity and smoothness of  $\eta(\theta, \zeta)$ , the equilibrium extensive variables are computed in the following form

$$(2.1) \quad \eta = -\partial\sigma/\partial\theta, \quad \gamma = -\partial\sigma/\partial\zeta, \quad \varepsilon = \sigma - \theta\partial\sigma/\partial\theta - \zeta\partial\sigma/\partial\zeta,$$

where

$$\sigma(\theta, \zeta) = \min_{\varepsilon, \gamma} \{ \varepsilon - \theta\eta(\varepsilon, \gamma) - \zeta\gamma \}.$$

Having in mind that  $\sigma$  being a minimum of linear functions, is a concave function of  $\{\theta, \zeta\}$ , the following inequalities hold

$$(2.2) \quad \frac{\partial^2\sigma}{\partial\theta^2} \leq 0, \quad \frac{\partial^2\sigma}{\partial\zeta^2} \leq 0, \quad \frac{\partial^2\sigma}{\partial\theta^2} \frac{\partial^2\sigma}{\partial\zeta^2} \geq \left( \frac{\partial^2\sigma}{\partial\theta\partial\zeta} \right)^2.$$

Consider the reversible process of the surface  $\Gamma$  dilatation that implies the entropy maximum principle fulfillment at each instant of time. Hence, the formulae

$$d\varepsilon - \theta d\eta - \zeta d\gamma = 0, \quad \varepsilon - \theta\eta - \zeta\gamma = \sigma$$

are valid, whence

$$\theta d(A\eta) = d(A\varepsilon) - \zeta d(A\gamma) + \sigma dA.$$

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The last term of this expression coincides with the dilatation work, that is why  $\sigma$  is the surface tension coefficient.

Note that the positivity condition  $\sigma > 0$  is necessary for the stability of interface  $\Gamma$  which could be only tensile. On the contrary, liquids in contact with  $\sigma < 0$  must be mutually soluble. Nevertheless, the abundant quantities  $\eta$ ,  $\gamma$  and  $\varepsilon$  are not necessarily positive because of the inactive substances which tend to leave surface  $\Gamma$  and should be included in the class of surfactants. Therefore, the signs of  $\partial\sigma/\partial\theta$ ,  $\partial\sigma/\partial\zeta$  may be arbitrary, but conditions (2.2) must be always valid because they express the entropy maximum principle. At first sight, the first of inequalities (2.2) contradicts to [15], where the surface tension minimum with respect to the temperature has been established for the aqueous long chain alcohol solutions. In fact, it was obviously measured that the compound function  $\widehat{\sigma}(\theta) = \sigma(\theta, \zeta(\theta))$ , where the variable chemical potential  $\zeta = \zeta(\theta)$  of alcohol is to be computed from the condition  $N = \text{constant}$ . Of course,  $\widehat{\sigma}(\theta)$  could have a minimum for the concave function  $\sigma(\theta, \zeta)$  provided that chemical potential  $\zeta$  decreases rather fast when temperature  $\theta$  increases. In other words, the rise of the temperature could also initiate the concomitant process of leaving of surfactant molecules off the surface  $\Gamma$ , which causes the resulting increment of  $\sigma$ . This proves the contention.

Conformably to the bulk phases, let us introduce the specific internal energy  $e$  and concentration  $c$  of surfactants, and define the following concave function

$$f(\theta, \zeta) = \min_{e, c} \{e - \theta s(e, c) - \zeta c\},$$

where specific entropy  $s = s(e, c)$  is regarded as a given function of extensive variables  $e, c$ . Function  $f(\theta, \zeta)$  coincides with the specific Gibbs potential [17], and the use of the entropy maximum principle leads to the formulae

$$(2.3) \quad s = -\partial f / \partial \theta, \quad c = -\partial f / \partial \zeta, \quad e = f - \theta \partial f / \partial \theta - \zeta \partial f / \partial \zeta.$$

Assuming the strict concavity of  $f(\theta, \zeta)$ , one obtains the important inequalities

$$(2.4) \quad \frac{\partial^2 f}{\partial \theta^2} < 0, \quad \frac{\partial^2 f}{\partial \zeta^2} < 0, \quad \frac{\partial^2 f}{\partial \theta^2} \frac{\partial^2 f}{\partial \zeta^2} > \left( \frac{\partial^2 f}{\partial \theta \partial \zeta} \right)^2.$$

Since formulae (2.1), (2.2) are completely similar to (2.3), (2.4), the surface tension coefficient  $\sigma$  coincides with the surface Gibbs potential.

### 3. Governing equations

For simplicity, let us conjecture that the temperature and the small concentration of surfactant molecules do not influence the dynamic characteristics of the ambient and drop fluids, i. e. the fluid density  $\rho$  and viscosity  $\mu$  have piece-wise constant values with the discontinuity surface  $\Gamma$ . The Navier-Stokes equations and boundary conditions, written once in non-inertial coordinate system  $(\mathbf{x}, t)$  connected with the position  $\mathbf{z}(t)$  of the drop mass centre in an inertial coordinate system, take the following form:

$$(3.1) \quad \rho \frac{d\mathbf{v}}{dt} = \rho \mathbf{g} - \rho \frac{d^2 \mathbf{z}}{dt^2} - \text{div } \mathbf{P}, \quad \text{div } \mathbf{v} = 0 \text{ outside } \Gamma,$$

$$(3.2) \quad [\mathbf{P} \cdot \mathbf{n}] = \text{div}_\Gamma (\sigma \nabla_\Gamma \mathbf{x}), \quad \frac{d\mathbf{x}}{dt} = \mathbf{v}, \quad [\mathbf{v}] = 0 \text{ on } \Gamma,$$

$$(3.3) \quad \mathbf{v} \rightarrow -\frac{dz}{dt}, \quad p - \mathbf{x} \cdot \nabla p \rightarrow 0 \quad \text{when } |x| \rightarrow \infty,$$

$$(3.4) \quad \mathbf{v} = 0, \quad \mathbf{z} = 0, \quad \frac{dz}{dt} = 0, \quad \Gamma = \{|\mathbf{x}| = a\} \quad \text{when } t = 0.$$

Here the denotations for velocity  $\mathbf{v}$ , pressure  $p$ , pressure tensor  $\mathbf{P} = p\mathbf{I} - 2\mu(\nabla\mathbf{v})_{\text{sym}}$ , normal  $\mathbf{n}$ , and average radius  $a$  of the drop are introduced. Square brackets denote the function's jump on  $\Gamma$  (outer minus inner), viz.,

$$[F] = F_+ - F_-, \quad F_{\pm}(\mathbf{x}) = \lim_{\delta \rightarrow \pm 0} F(\mathbf{x} + \delta\mathbf{n}(\mathbf{x})).$$

Subscript  $\Gamma$  corresponds to the surface differential operators.

In virtue of the well-known formula  $\Delta_{\Gamma}\mathbf{x} = \kappa\mathbf{n}$ , where  $\kappa$  is the sum of the principal curvatures of  $\Gamma$ , the Laplace formula  $[p] = \sigma\kappa$  in an equilibrium state follows from the first equation of (3.2) [19]. In a general case, the surface gradient of  $\sigma$  evokes the Marangoni convection [18]. The second equation (3.2) implies the surface  $\Gamma$  to be material, and, in particular, phase transitions to be absent.

Let  $\mathbf{q}, \mathbf{j}$  be the heat and surfactant fluxes in the bulk phases, and  $\mathbf{q}_{\Gamma}, \mathbf{j}_{\Gamma}$  be the corresponding surface fluxes along the interface  $\Gamma$ . Then, the differential conservation laws of energy and surfactant molecules take the following form [19, 20]:

$$(3.5) \quad \rho \frac{de}{dt} = 2\mu |(\nabla\mathbf{v})_{\text{sym}}|^2 - \text{div } \mathbf{q} \quad \text{outside } \Gamma,$$

$$(3.6) \quad \rho \frac{dc}{dt} = -\text{div } \mathbf{j} \quad \text{outside } \Gamma,$$

$$(3.7) \quad \frac{d\varepsilon}{dt} + \varepsilon \text{div}_{\Gamma} \mathbf{v} = \sigma \text{div}_{\Gamma} \mathbf{v} - [\mathbf{q} \cdot \mathbf{n}] - \text{div}_{\Gamma} \mathbf{q}_{\Gamma} \quad \text{on } \Gamma,$$

$$(3.8) \quad \frac{d\gamma}{dt} + \gamma \text{div}_{\Gamma} \mathbf{v} = -[\mathbf{j} \cdot \mathbf{n}] - \text{div}_{\Gamma} \mathbf{j}_{\Gamma} \quad \text{on } \Gamma.$$

Assuming that the Onsager principle [6] is valid for both the bulk and surface fluxes one can obtain the following phenomenological relations

$$\begin{aligned} -\mathbf{h} &= K^{11}\nabla\theta + K^{12}\nabla\zeta, & -\mathbf{j} &= K^{21}\nabla\theta + K^{22}\nabla\zeta, \\ -\mathbf{h}_{\Gamma} &= \kappa^{11}\nabla_{\Gamma}\theta + \kappa^{12}\nabla_{\Gamma}\zeta, & -\mathbf{j}_{\Gamma} &= \kappa^{21}\nabla_{\Gamma}\theta + \kappa^{22}\nabla_{\Gamma}\zeta, \end{aligned}$$

where the bulk and surface entropy fluxes

$$\mathbf{h} = (\mathbf{q} - \zeta\mathbf{j})/\theta, \quad \mathbf{h}_{\Gamma} = (\mathbf{q}_{\Gamma} - \zeta\mathbf{j}_{\Gamma})/\theta$$

are introduced, and matrices  $\{K^{ij}\}, \{\kappa^{ij}\}$  are symmetrical and positive definite.

Using the new more suitable denotations

$$\begin{aligned} \tau_1 &= \theta, \quad \tau_2 = \zeta, \quad \tau = \{\tau_1, \tau_2\}, \\ A^{ij} &= -\frac{\partial^2 f}{\partial \tau_i \partial \tau_j}, \quad \alpha^{ij} = -\frac{\partial^2 \sigma}{\partial \tau_i \partial \tau_j}, \quad \sigma^i = \frac{\partial \sigma}{\partial \tau_i}, \\ \Phi^1 &= \{K^{11} |\nabla\theta|^2 + 2K^{12} \nabla\theta \cdot \nabla\zeta + K^{22} |\nabla\zeta|^2 + 2\mu |(\nabla\mathbf{v})_{\text{sym}}|^2\}/\theta, \\ \Phi_{\Gamma}^1 &= \{\kappa^{11} |\nabla_{\Gamma}\theta|^2 + 2\kappa^{12} \nabla_{\Gamma}\theta \cdot \nabla_{\Gamma}\zeta + \kappa^{22} |\nabla_{\Gamma}\zeta|^2\}/\theta, \end{aligned}$$

$$\Phi^3 = 0, \quad \Phi_{\Gamma}^2 = 0,$$

eqs (3.5)-(3.8) become

$$(3.9) \quad \rho A^{ij} \frac{d\tau_j}{dt} = \text{div} (K^{ij} \nabla \tau_j) + \Phi^i \quad \text{outside } \Gamma,$$

$$(3.10) \quad \alpha^{ij} \frac{d\tau_j}{dt} = \sigma^i \text{div}_{\Gamma} \mathbf{v} + \left[ K^{ij} \frac{\partial \tau_j}{\partial n} \right] + \text{div}_{\Gamma} (\kappa^{ij} \nabla_{\Gamma} \tau_j) + \Phi_{\Gamma}^i, \quad [\tau_i] = 0 \quad \text{on } \Gamma,$$

where Einstein's summation convention on repeated indices is adopted. The continuity conditions for  $\{\theta, \zeta\}$ , following from the local thermodynamic equilibrium principle, and, in particular, giving the Langmuir formula [2], are also added in equations (3.10). It is obvious that the system of equations (3.9)-(3.10) has a symmetrical form with positive definite matrices  $\{A^{ij}\}$ ,  $\{K^{ij}\}$ ,  $\{\alpha^{ij}\}$ ,  $\{\kappa^{ij}\}$ .

#### 4. Linear problem

Let us denote the piece-wise constant kinematic viscosity coefficient  $\nu = \mu/\rho$  for each liquid, and introduce the dimensionless parameter  $\delta = \max\{|\rho|g|\alpha^3/\mu\nu\}$  which is supposed to tend to zero. For  $\delta=0$ , the evident prime solution of equations (3.1)-(3.4), (3.9), (3.10) is

$$\mathbf{v} = 0, \quad p = \begin{cases} 2\sigma/a & \text{for } |\mathbf{x}| < a \\ 0 & \text{for } |\mathbf{x}| > a \end{cases}, \quad \tau_i = \text{const}, \quad \Gamma = \{|\mathbf{x}| = a\}.$$

Expanding the origin solution in a power series about  $\delta=0$ , substituting it in the governing equations, collecting the terms in  $\delta^n$ , and requiring them to vanish, the infinite recurrence system of equations is resulted. In order to obtain the first linear term of the series, it suffices to linearize equations (3.1)-(3.4), (3.9), (3.10) at the prime solution. Retaining the same notations for the disturbed quantities  $\tau_i$ ,  $p$ , and  $\mathbf{P}$ , the following linear problem becomes

$$\frac{\partial \mathbf{v}}{\partial t} = \mathbf{g} - \frac{d^2 \mathbf{z}}{dt^2} - \frac{1}{\rho} \nabla p + \nu \Delta \mathbf{v}, \quad \text{div } \mathbf{v} = 0 \quad \text{outside } \Gamma,$$

$$[\mathbf{P} \cdot \mathbf{n}] = \text{div}_{\Gamma} (\alpha^i \tau_i \nabla_{\Gamma} \mathbf{x}), \quad [\mathbf{v}] = 0, \quad \mathbf{v} \cdot \mathbf{n} = 0 \quad \text{on } \Gamma,$$

$$\mathbf{v} \rightarrow -\frac{d\mathbf{z}}{dt}, \quad p - \mathbf{x} \cdot \nabla p \rightarrow 0 \quad \text{when } |\mathbf{x}| \rightarrow \infty,$$

$$\rho A^{ij} \frac{\partial \tau_j}{\partial t} = K^{ij} \Delta \tau_j \quad \text{outside } \Gamma,$$

$$\alpha^{ij} \frac{\partial \tau_j}{\partial t} = \sigma^i \text{div}_{\Gamma} \mathbf{v} + \left[ K^{ij} \frac{\partial \tau_j}{\partial n} \right] + \kappa^{ij} \Delta_{\Gamma} \tau_j, \quad [\tau_i] = 0 \quad \text{on } \Gamma,$$

$$\mathbf{v} = 0, \quad \mathbf{z} = 0, \quad \frac{d\mathbf{z}}{dt} = 0, \quad \tau_i = 0 \quad \text{when } t = 0.$$

Matrices  $\{A^{ij}\}$ ,  $\{K^{ij}\}$ ,  $\{\alpha^{ij}\}$ ,  $\{\kappa^{ij}\}$ , and values  $\{\sigma^i\}$ , computed at the equilibrium state, are constant. At once, the existence of the exact solution with spherical interface  $\Gamma = \{|\mathbf{x}| = a\}$  was taken into consideration [1].

In order to avoid the cumbersome calculations, let us temporally limit our scope

of investigation by assuming that  $\mathbf{g} = g(t)\mathbf{w}$ , where  $\mathbf{w}$  is a constant unit vector. Having introduced the spherical coordinates  $(r, \vartheta, \varphi)$  defined by  $r = |\mathbf{x}|$ ,  $\cos \vartheta = \mathbf{w} \cdot \mathbf{x}/a$ , and supposing the axial symmetry of the flow field, one obtains the following representation of the solution

$$v_r = -\frac{2}{r}\psi(r, t)\cos \vartheta, \quad v_\vartheta = \frac{1}{r}\frac{\partial\{r\psi(r, t)\}}{\partial r}\sin \vartheta,$$

$$\tau_i = \chi_i(r, t)\cos \vartheta, \quad \mathbf{z} = z(t)\mathbf{w},$$

where  $\psi(r, t)$ ,  $\chi_i(r, t)$ ,  $z(t)$  are the unknowns. After using the Laplace transformation with respect to time (denoted by an asterisk), we obtained the following coupled system of equations

$$(4.1) \quad L^2(\nu L^2 \psi^* - \lambda \psi^*) = 0 \quad \text{for } r \neq a,$$

$$\psi^* = 0, \quad [\psi^*] = 0, \quad [\partial \psi^* / \partial r] = 0,$$

$$(4.2) \quad [\mu \partial^2 \psi^* / \partial r^2] = \sigma^i \chi_i^* / a \quad \text{at } r = a,$$

$$(4.3) \quad \partial \psi^* / \partial r, \psi^* / r \rightarrow \lambda z^* / 2 \quad \text{as } r \rightarrow \infty,$$

$$(4.4) \quad \rho \lambda A^{ij} \chi_j^* = K^{ij} L^2 \chi_j^* \quad \text{for } r \neq a,$$

$$(4.5) \quad \lambda a^{ij} \chi_j^* = 2\{\sigma^i \partial \psi^* / \partial r + \kappa^{ij} \chi_j^* / a\} / a + [K^{ij} \partial \chi_j^* / \partial r], \quad [\chi_j^*] = 0 \quad \text{at } r = a,$$

$$(4.6) \quad a[\rho](g^* - \lambda^2 z^*) = [\partial\{r(\mu L^2 \psi^* - \rho \lambda \psi^*) / \partial r\} - 2\sigma^i \chi_i^* / a] \quad \text{at } r = a.$$

Here  $L^2 f = \frac{1}{r^2} \left\{ \frac{\partial}{\partial r} \left( r^2 \frac{\partial f}{\partial r} \right) - 2f \right\}$ ; normal  $\mathbf{n}$  is equal to  $\mathbf{x}/a$  (that defines completely a jump); the initial conditions (3.4) were taken into consideration.

Equation (4.6), which follows from the normal component of the dynamic condition, can be rewritten in the compact form

$$(4.7) \quad a^3[\rho](g^* - \lambda^2 z^*) = G,$$

where

$$G = \lim_{r \rightarrow \infty} r^4 \frac{\partial}{\partial r} \left\{ \frac{1}{r} (\mu L^2 \psi^* - \rho \lambda \psi^*) \right\}.$$

Actually, the integral identity

$$G = \int_0^\infty r^3 L^2 (\mu L^2 \psi^* - \rho \lambda \psi^*) dr + a^4 \left[ \frac{\partial}{\partial r} \left\{ \frac{1}{r} (\mu L^2 \psi^* - \rho \lambda \psi^*) \right\} \right]$$

gives the following expression of the right-hand side of equation (4.6)

$$G/a^2 + 2\{[\mu L^2 \psi^* - \rho \lambda \psi^*] - \sigma^i \chi_i^* / a\}.$$

Rearranging, and using (4.2), one obtains (4.7).

The solution of equations (4.1) could be obviously represented in the following form [1, 23]

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$$\psi^*(r, \lambda) = \lambda z^*(\lambda)r/2 + C_1(\lambda)/r^2 + C_2(\lambda)H(r\sqrt{\lambda/v_+}) \quad \text{for } r > a,$$

$$\psi^*(r, \lambda) = C_3(\lambda)r + C_4(\lambda)H(r\sqrt{\lambda/v_-}) \quad \text{for } r < a,$$

where the function  $H(\omega)$  is to be chosen as  $(e^{-\omega/\omega})'$  for  $r > a$ , and as  $(\sin \omega/\omega)'$  for  $r < a$  (the primes denote the derivatives);  $v_+$ ,  $v_-$  are the viscosities of the ambient and drop liquids respectively (in accordance with the choice of the normal  $\mathbf{n}$ ). Boundary conditions (4.2)-(4.3) are to yield the unknown functions  $C_k(\lambda)$  in terms of  $z^*(\lambda)$  and  $\chi_i^*(r, \lambda)$ . Note that  $G = 3\rho_+ \lambda C_1(\lambda)$ , therefore, in order to obtain the equation for  $z(t)$ , it is necessary to find  $C_1(\lambda)$ , and to substitute it into equation (4.7).

Analogous to the preceding, the solution of equations (4.4) has the representation

$$\chi_i^*(r, \lambda) = E_i^m \frac{H(r\sqrt{\lambda/\lambda_m})}{H(a\sqrt{\lambda/\lambda_m})} F_m^i D_j(\lambda),$$

where  $\{\lambda_m\}$  are the roots of the characteristic polynomial  $\det(\rho\lambda A^{ij} - K^{ij})$ ; matrix  $\{E_i^m\}$  is defined by the equations

$$(\rho\lambda_m A^{ij} - K^{ij})E_i^m = 0,$$

and  $\{F_m^i\} = \{E_i^m\}^{-1}$ . It is obvious that such matrices as  $\{E_i^m\}$ ,  $\{F_m^i\}$  exist and the numbers  $\{\lambda_m\}$  are positive, because the constant matrices  $\{A^{ij}\}$ ,  $\{K^{ij}\}$  are symmetrical and positively definite. Of course, this construction is to be independently done for the ambient and drop liquids. The functions  $D_i(\lambda)$  equaling to  $\chi_i^*(a, \lambda)$ , are determined from boundary conditions (4.5) which involve  $\psi^*(r, \lambda)$ .

Omitting stereotyped, but cumbersome calculations, totally analogous to those in [1], let us write the ultimate formula for the Laplace image  $z^*(\lambda)$  of the mass centre position

$$(4.8) \quad m^*(\lambda)\lambda^2 z^*(\lambda) = (\rho_0 - \rho)g^*(\lambda).$$

Hereafter subscript "zero" corresponds to the drop characteristics, and the following denotations are introduced

$$m^*(\lambda) = \rho_0 + \frac{\rho}{2} + \frac{9M^*(\lambda)}{2a^2\lambda},$$

$$\frac{1}{M^*(\lambda)} = \frac{1}{\mu X(a\sqrt{\lambda/v})} + \frac{1}{2\mu + 3\mu_0 X_0(a\sqrt{\lambda/v_0}) + 2Q(\lambda)},$$

$$Q(\lambda) = Q_{ij}(\lambda)\sigma^i\sigma^j,$$

where the matrix  $\{Q_{ij}\}$  is inverse to the matrix with elements

$$R^{ij}(\lambda) = \lambda a \alpha^{ij} + \frac{2}{a} \chi^{ij} + 2K^{ik} E_k^m Z(a\sqrt{\lambda/\lambda_m}) F_m^j + K_0^{ik} E_{0k}^m Z_0(a\sqrt{\lambda/\lambda_{0m}}) F_{0m}^j,$$

$$X(\omega) = 1 + \omega, \quad X_0(\omega) = \frac{(6 + \omega^2)\omega - 3(2 + \omega^2) \tanh \omega}{3[(3 + \omega^2) \tanh \omega - 3\omega]},$$

$$Z(\omega) = 1 + \frac{\omega^2}{2(1 + \omega)}, \quad Z_0(\omega) = \frac{(2 + \omega^2) \tanh \omega - 2\omega}{\omega - \tanh \omega}.$$

### 5. Discussion

First of all, we would like to note that the assumption of the axial symmetry of the flow is not necessary because the principle of superposition is surely valid for linear systems [21]. Consequently, formula (4.8) may be rewritten in a vectorial form. It is worthwhile to remark that formula (4.8) could be also interpreted as Newton's law

$$(5.1) \quad m * \frac{d^2z}{dt^2} = (\rho_0 - \rho)g,$$

where the "drop mass"  $m(t)$  plays now a role of a nonlocal convolution operator with the Laplace image  $m^*(\lambda)$ , viz.,

$$\left(m * \frac{d^2z}{dt^2}\right)(t) = \left(\rho_0 + \frac{\rho}{2}\right) \frac{d^2z}{dt^2}(t) + \frac{9}{2^2 a} \int_0^t M(t-\xi) dz(\xi),$$

where  $M(t)$  has the image  $M^*(\lambda)$ . This formula transfers to the usual expression for the augmented mass when the viscosities vanish and the surface tension is constant.

Matrix  $\{R^{ij}\}$  is positive definite, therefore,  $Q(\lambda) > 0$  for whichever values  $\{\sigma^i\}$  not equal to zero. That leads to the increment of  $M^*(\lambda)$  and, consequently, to the deceleration of the drop motion in comparison with a drift in a pure ambient liquid. In other words, Le Chatelier's principle due to the fundamental thermodynamic laws, is proven for arbitrary surfactant. Moreover, this approach does not depend on the number of variables  $\{\tau_i\}$ , i. e., formula (4.8) retains for the case of several surfactants.

Taking into consideration the identities

$$X(0) = X_0(0) = Z(0) = Z_0(0) = 1,$$

and using (4.8), the large-time asymptotics of the mass centre speed is readily computed for the constant gravitation  $g$

$$(5.2) \quad \frac{dz}{dt} = \frac{3\mu + 3\mu_0 + 2\beta}{2\mu + 3\mu_0 + 2\beta} \frac{2a^2}{9\mu} (\rho_0 - \rho)g + O(t^{-1/2}),$$

where

$$\beta = Q(0) \text{ and } R^{ij}(0) = -\frac{2}{a} \kappa^{ij} + 2K^{ij} + K_0^{ij}.$$

For  $\beta=0$ , (5.2) is the well-known formula obtained by Hadamard [13] and Rybczynski [22]. In another extreme case  $\beta \rightarrow \infty$ , the limit of (5.2) coincides with that when  $\mu_0 \rightarrow \infty$ , i. e., the reactive capillary forces make the effect of the drop viscosity increment (see the detailed discussion in [16]).

In conclusion, note that the equation for the mass centre of a drop driven by both the buoyancy and capillary forces, could similarly be derived. Using the principle of superposition, one obtains Newton's equation like (5.1) whose right-hand side contains the additional active capillary force  $f_\sigma$  having the Laplace image

$$f_\sigma^* = -\frac{3}{a} R^*(\lambda) \sigma^i W_i(\lambda) / \lambda.$$

Here

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$$R^*(\lambda) = \frac{\mu X(a\sqrt{\lambda/v})}{2\mu + \mu X(a\sqrt{\lambda/v}) + 3\mu_0 X_0(a\sqrt{\lambda/v_0}) + 2Q(\lambda)}$$

$$W_i(\lambda) = w_i + Q_{ij}(\lambda)(K^{jk} - K_0^{jk})w_k,$$

and  $w_i$  is a constant initial gradient of  $\tau_i$  (i. e.,  $\tau_i = w_i \cdot x$  at  $t=0$ ) being supposed to be sufficiently small, more precisely,  $\max\{|\sigma^i w_i|/a/\sigma\} \ll 1$ . Note that  $f_c^*$  tends to carry away the drop to the region of the smallest surface tension, i. e., it minimizes the Gibbs thermodynamic potential.

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