<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Author(s)</th>
<th>Citation</th>
<th>Issue Date</th>
<th>Doc URL</th>
<th>Rights</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SPH simulations of binary droplet deformation considering the Fowkes theory</td>
<td>Natsui, Shungo; Tonya, Kazui; Nogami, Hiroshi; Kikuchi, Tatsuya; Suzuki, Ryosuke O.</td>
<td>Chemical Engineering Science, 229, 116035</td>
<td>2021-01-16</td>
<td><a href="http://hdl.handle.net/2115/86549">http://hdl.handle.net/2115/86549</a></td>
<td>© [2021]. This manuscript version is made available under the CC-BY-NC-ND 4.0 license</td>
</tr>
</tbody>
</table>
SPH Simulations of binary droplet deformation considering the Fowkes theory

Shungo Natsui\textsuperscript{a)}*, Kazui Tonya\textsuperscript{b)}, Hiroshi Nogami\textsuperscript{a)}.

Tatsuya Kikuchi\textsuperscript{b)}, and Ryosuke O. Suzuki\textsuperscript{b)}

\textsuperscript{a)} Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Katahira 2-1-1, Aoba-ku, Sendai, 980-8577, Japan.

\textsuperscript{b)} Division of Materials Science and Engineering, Faculty of Engineering, Hokkaido University, Kita 13 Nishi 8, Kita-ku, Sapporo, 060–8628, Japan.

*Corresponding author. Tel.: +81–22–217–5157

E–mail address: natsui@tohoku.ac.jp
Abstract:

To analyze the complex droplet transient deformation involving two immiscible phases, a practical multi-interfacial tension model has been introduced in the SPH framework. The attraction, which operates on the interface between the different phases is explicitly defined as London dispersion force using the Fowkes theoretical model, and the interfacial tension can be calculated using the sum of the attraction magnitudes corresponding to the surrounding particles. The analytical solution demonstrated good agreement with the simulated results corresponding to the macroscopic multicontact angles and nature of interphase interfacial forces. This simple model is widely applicable to the dynamic analysis of capillary forces involving two or more liquids, and we demonstrated its application to the simulation of the deformation behavior of a binary droplet that contacts a solid. The solid-liquid-liquid contact angle is not sufficient to predict the equilibrium morphology, and the momentum exchange between the two liquids should be considered.

Keywords: SPH; binary droplet; interfacial tension; Fowkes hypothesis;
1. Introduction

The interfacial morphology of two immiscible liquids on a solid surface in a gaseous environment plays an essential role in many industrial processes such as spray combustion in liquid-fuel engines, various food-processing mixing operations, and the processing of petroleum in the context of dispersed water droplets in crude oil. In particular, in pyrometallurgical processes, the interfacial flow of high-temperature liquid-metal-based phase-molten oxides (slag) on the solid materials must be strictly controlled to enhance the smelting efficiency; the base metals in such processes include iron, copper, aluminum, tin, and lead.

In the copper smelting process, various forms of molten copper sulfide (matte) - molten slag – solid magnetite as the dispersed phase have been observed, and it is expected that the reaction between several pairs of liquids is dominated by the interphase boundary area (Kemori et al., 1989; Fernández-Caliani et al., 2012; Pérez-Tello et al., 2018). In addition, some noble metals (such as gold and platinum) are also concentrated in the matte, and their loss has a potentially significant economic impact. Although matte and slag are passing at the bottom of the flash smelting furnace, matte droplets containing noble metals remain in the slag phase in the case of insufficient separation, leading to the noble metals in the slag phase being discarded.
Despite its notable economic importance, the transient behavior of the interfacial boundary between the matte and slag has yet to be extensively investigated because direct observation of the dynamic behavior of a molten matte–slag boundary is difficult owing to the presence of an extremely limited observation domain (Sauerland et al., 1993; Chung and Cramb, 2000; Fagerlund and Jalkanen, 2000; Han and Holappa, 2003; Bellemans et al., 2017). Conventionally, the morphology of matte–slag liquids has been discussed on the assumption of a core-shell type in which the slag encompasses the matte based on the shape obtained after solidification in equilibrium experiments (Kemori et al, 1989). When droplets of two immiscible liquids immersed in gaseous phase are generally divided to contact three equilibrium topologies, the following three conditions may occur depending on the interfacial tensions balance between the three fluids: (i) The droplets may remain separated (non-engulfing configuration), (ii) one of the phases may completely cover the other one (complete engulfing, which corresponds to the core-shell structure), or (iii) a doublet of droplets may form (partial engulfing) (Torza and Mason, 1970; Pannacci, 2008; Guzowski, 2012). Although this model has succeeded in simplifying the interfacial morphology representation, it is a limited ideal system, and the momentum exchange between two liquids having different physical properties must be considered. The interphase dynamics that involves material
discontinuity and force coupling across the interface between different phases has been commonly observed; it, however, represents a challenging topic in terms of numerical modelling and process accounting.

Numerical simulations based on the multiphysics model can be used as a powerful tool for predicting the behavior of various melts (Natsui et al., 2017; 2020a; 2020b). Several numerical simulations have been carried out to understand the heat and mass transfer phenomena pertaining to dispersed molten sulfide matte–molten oxide slag phases in the commercial furnace (Kemori, et al., 1990; Sasaki et al., 2009).

Large-scale simulations, which could be realized owing to the evolution of computational capacity in recent years, are expected to further improve the space resolution and analytical accuracy, and their use would undoubtedly be valuable in the industry. To enable its application to a system with several two-liquids, it is necessary to solve the dynamic form of the droplet with a small calculation load. In recent numerical studies focusing on the collision of immiscible binary droplets, the most common techniques for such calculation include the volume of fluid method (Hoffmann, 2006; Pan and Suga, 2005; Tang, 2016), level set method (Tanguy and Berlemont, 2005), and lattice Boltzmann method (Liang, 2016; Sadullah, 2018; Abadi, 2018). These grid-based Eulerian computational fluid dynamics methods have been used to directly solve the
multiphase Navier–Stokes equations. They require computationally expensive interface tracking techniques by introducing an additional field variable defining the position of the interface (Katopodes, 2019). In these methods, explicit tracking of the fluid interface is avoided at the cost of solving an additional hyperbolic equation for the field variable. In these grid-based Eulerian approaches, the main objective is to improve the accuracy of prediction of the evolution of a moving interface. However, these approaches are likely not suitable for the large deformation problem of two or more liquids accompanying severe scattering. Because these models are based on the discretization scheme of space with tetragonal meshes and the interface crosses the interior of the lattice, it is difficult to completely eliminate the numerical diffusion of interfacial shapes across the cell to deal with dispersed phases. Alternatively, as a mesh-free particle method, the smoothed particle hydrodynamics (SPH) method can effectively avoid the abovementioned mesh distortion problem and offer excellent flexibility for simulating the large deformation of liquids (Lucy, 1977; Monaghan, 1988; 1989; 1992; 1994; 2012; Breinlinger, 2013; Yang, 2014). The SPH method is a fully Lagrangian approach that discretizes fluid by moving particles. This approach provides an intuitive description of the fluid flow, because it does not require the consideration of interfacial numerical diffusion even for the dispersed phase. Fortunately, the calculation algorithm (for a
weakly compressible viscous flow) can be remarkably simple if a fully explicit time integration procedure is employed.

Recently, SPH has been often applied for the description of multiple-fluid flow dynamics by using various improved interfacial representations. Several interfacial tension formulations have been developed to deal with multiphase fluid flow problems, most of which are based on the continuum surface force (CSF) method (Brackbill et al., 1992; Morris, 2000; Hu and Adams, 2006; Rezavand, 2018) or the Cahn–Hilliard model (Cahn and Hilliard, 1958; He et al., 2014). However, this well-known mesh-based interfacial tension model has several issues when applied to a mesh-free particle-based framework, such as the presence of errors in the interfacial curvature calculation and negative pressure contribution, as specified in previous study by Krimi et al. (2018).

Although it is necessary to suitably calculate the local interfacial curvature from particle positions, the small number of particles at the interface may limit the computational accuracy in the case of many dispersed droplets being considered under limited computer resources; this problem exists even the number of particles is increased to a satisfactory level, as long as a new interface appears. Furthermore, this approach cannot be easily applied to cases in which the interfacial tension changes locally, such as a Marangoni flow, because the interfacial force component acting tangentially to the
surface is ignored in the CSF model (Inagaki, 2018). An alternative formulation of the interfacial tension for the SPH is based on microscopic interphase attractive potentials (Tartakovsky and Meakin, 2005; Kordilla et al., 2013; Li et al., 2018), this approach involves assigning interfacial particles attractive/repulsive forces based on pairwise forces inspired by the molecular origin of the interfacial tension phenomena. Defining these forces to reproduce the effects of interfacial tension led to promising results in several cases involving droplets and flow on a complex solid (Shigorina et al., 2017). Unfortunately, the critical issue of this “potential model” is that the resulting surface tension needs to be calibrated. Although the relationship between interparticle force and interfacial energy has been clarified theoretically (Kondo et al., 2007; Tartakovski and Panchenko, 2016; Nair and Pöschel, 2018), it is not able to be convincingly stated that the verification of calculation and theoretical results has been performed adequately for multiliquid systems. If the interfacial tension between multiple phases can be calculated using a potential model, this technique can be easily applied to a wide range of fields of large-scale systems.

To this end, the objectives of the present research are to develop the abovementioned approach for a model that considers multiphase interfacial energy and to verify the computational accuracy of the model based on a comparison of the
analytical and theoretical results.

2. Numerical methods

2.1. Basic formulation of SPH

The basic concept of the SPH assumption is the introduction of a kernel function as an integral interpolation to solve a differential equation, such that the fluid dynamics is represented by a set of particle motion equations (Monaghan, 1994); in other words, the formulation is based on an interpolation scheme that allows the estimation of a vector or scalar function $f$ at position $r$ in terms of the values of the function at the discretization points.

$$f(r) \equiv \int f(r')W(r - r', h)dV,$$

where $r$ and $r'$ denote arbitrary coordinates, $V$ denotes the volume, and $W$ is the smoothing kernel function with being the radius of influence. The gradient form of Eq. (1) can be represented as follows:

$$\nabla f(r) \equiv \int \nabla f(r')W(r - r', h)dV. \tag{2}$$

This form can be expanded by partial integration as

$$\nabla f(r) \equiv \int \nabla(f(r')W(r - r', h))dV - \int f(r')\nabla W(r - r', h)dV. \tag{3}$$

In the general SPH scheme, the first term on the right-hand side can be converted to the
boundary integral of the following equation by using the divergence theorem; thus, the
kernel function $W(r - r', h) = 0$ on the boundary and $\nabla f(r)$ can be expressed as

takes:

$$\nabla f(r) \approx - \int f(r') \nabla W(r - r', h) dV. \quad (4)$$

Generally, this is referred to as the final discretization equation in the standard SPH
method. Unfortunately, this assumption does not yield in sufficiently accurate solution
in the vicinity of the phase boundary. When applying this approximation to dispersed
fluids, the discontinuities in the density distribution of the fluids become significant,
which leads to an increase in the numerical errors. The moving least squares (MLS)
method is widely employed for approximating the function to solve this problem
(Colagrossi and Landrini, 2003), which is related to the numerical fluctuations in the
pressure at the nearby interface. The pressure is a function of the local density, and thus,
the smooth density field of a bulk phase leads to a continuous pressure distribution. The
MLS method improves the mass–area–density consistency and filters small-scale
pressure oscillations, as described briefly in the subsequent section.

2.2. Density approximation

Owing to the compactness, the summation in the function can be replaced with a
summation over particles only within the distance \(h\) from \(\mathbf{r}_i\); thus, \(W(\mathbf{r}_{ij}, h) = 0\) when \(|\mathbf{r}_{ij}| > h\). The kernel must possess a symmetrical form to \(|\mathbf{r}_{ij}| > 0\). Here, \(i\) is the particle index, and \(j\) is the index of the neighboring particle around \(i\). The kernel has at least a continuous first derivative and must satisfy the normalization condition,

\[
\int W(\mathbf{r}_{ij}, h) d\mathbf{r} = 1.
\]

In the \(h \to 0\) limit, the kernel must be reduced to a Dirac delta function \(\delta(\mathbf{r}_{ij})\). Wendland’s kernel can be applied to avoid various kernel artifacts in a multiphase system (Wendland, 1995; Szewc et al., 2013).

\[
W(\mathbf{r}_{ij}, h) = \frac{21}{16\pi h^3} \left\{ \begin{array}{ll}
(1 - \frac{q}{2})^4 (2q + 1), & q < 2 \\
0, & q \geq 2,
\end{array} \right.
\quad (5)
\]

where \(|\mathbf{r}_{ij}|_0\) is the interparticle distance corresponding to the initial conditions, \(q = |\mathbf{r}_{ij}| / h\), and it was assumed that \(h = 1.05|\mathbf{r}_{ij}|_0\) (Natsui et al., 2012; 2014).

\(\rho_i\) is the density around particle, and \(\mathbf{r}_{ij}\) is a vector obtained from the difference between the density at particle \(i\) and the kernel functions of the \(N\) particles present within the radius of influence, as follows:

\[
\rho_i = \sum_{j=1}^{N} m_j W(\mathbf{r}_{ij}, h),
\quad (6)
\]

where the subscripts \(i\) and \(j\) denote the particle indices, \(m\) is the mass, \(\rho\) is the local density around particle, and \(\mathbf{r}_{ij}\) is a vector obtained from the difference between the
coordinates \( \mathbf{r}_i \) and \( \mathbf{r}_j \). Further, \( m_j \) is the mass of particle \( j \). Thus, the kernel function around particle \( i \) can be discretized using the following equation, which is derived from Eqs. (1), (2) and (3).

\[
f_i(\mathbf{r}) = \sum_{j=1}^{N} \frac{m_j}{\rho_j} f(\mathbf{r}_j) W(\mathbf{r}_{ij}, h).
\]  

(7)

In this manner, the gradient of \( f_i \) can be represented as follows:

\[
\nabla f_i(\mathbf{r}) = -\sum_{j=1}^{N} \frac{m_j}{\rho_j} f(\mathbf{r}_j) \nabla W(\mathbf{r}_{ij}, h).
\]

(8)

SPH is the attractive scheme for simulation of multiphase flows that involve rapidly changing interfaces between phases, because of its fully Lagrangian formulation. However, this advantage can be hindered and potentially offset by the possible occurrence of spurious interface fragmentations. This interface fragmentation artifact is especially troublesome in flows with high-density/high-viscosity ratio between fluid phases. In this study, the remedies available in the literature have been introduced in calculation model. The MLS involves first-order consistent gradient approximation, which allows the smoothing of pressure, and its first derivative values are obtained using the abovementioned method in the homogenous bulk phase (Szewc et al., 2013). The method of the least square interplant with constraint condition (CLS) represents an improved scheme, which leads to a more accurate approximation around the sampling
points than the MLS method does (Natsui et al., 2017; 2018). In the CLS method, by extending the moving least squares method in the one-dimensional error space for multiple dimensions, the particles can be made to represent a physical quantity directly. In the three-dimensional space, the CLS method approximates the values of various physical parameter around the particles. Refer to a previous report for parameters determining the procedure (Natsui et al., 2016).

2.3. Governing equations of liquid motion and discretization

This section provides the details regarding the SPH scheme for the discretization of the Navier–Stokes (N–S) equation governing a multiphase flow. The governing equations for a weakly compressible viscous flow are based on the relationship between the velocity of sound and the flow density under adiabatic conditions, as well as the N–S equations:

\[
\frac{Dp}{Dt} = c^2, \quad (9)
\]
\[
\rho \frac{D\mathbf{v}}{Dt} = -\nabla p + \mu \nabla^2 \mathbf{v} + \rho \mathbf{g} + \mathbf{F}_s \quad (10)
\]

where \(\mathbf{v}\) is the fluid velocity, \(p\) is the pressure, \(c\) is the velocity of sound, \(\mu\) is the viscosity, and \(\mathbf{F}_s\) is the interfacial force. On the right-hand side of Eq. (10), the first, second, third, and fourth terms denote the pressure gradient, viscous force, gravity, and
interfacial force, respectively. A density function is introduced such that it takes into account the boundary particles to smoothen each term. Subsequently, the N–S equation can be formulated considering the simple relationship \( \rho = m/V \) as follows:

\[
m_i \frac{Dv_i}{Dt} = -\sum_{j=1}^{N} \left( \langle p \rangle_i V_i^2 + \langle p \rangle_j V_j^2 + \Pi_{ij} \right) \nabla W_{ij}
\]

\[
+ \sum_{j=1}^{N} \frac{2\mu_i \mu_j}{\mu_i + \mu_j} \left( V_i^2 + V_j^2 \right) \frac{r_{ij}}{|r_{ij}|^2} (v_i - v_j) \nabla W_{ij} + m_i g + F_s,
\]

where \( \Pi \) is the artificial viscosity term, which is usually added to the pressure gradient term to help diffuse sharp variations in the flow and dissipate the energy of the high frequency term (Monaghan, 1988). The equation for the artificial viscosity is as follows:

\[
\Pi_{ij} = \begin{cases} 
-\alpha_1 \overline{c_{ij}} \varphi_{ij} + \alpha_2 \varphi_{ij}^2, & (v_i - v_j) \cdot r_{ij} < 0, \\
0, & (v_i - v_j) \cdot r_{ij} \geq 0 
\end{cases}
\]

\[
\varphi_{ij} = \frac{h(v_i - v_j) \cdot r_{ij}}{|r_{ij}|^2 + (0.1h)^2}
\]

where \( \overline{c_{ij}} \) and \( \overline{\rho_{ij}} \) denote the average values of the sound speed and the density, and \( \alpha_1 = \alpha_2 = 0.01 \) are assumed, respectively.

To determine the time derivative of pressure, Tait’s equation of state can generally be used (Monagan, 1994).

\[
\langle p \rangle_i = \frac{\gamma \rho_i^2 - \gamma \rho_i}{\rho_i - 1}
\]

where \( \gamma (= 7.0) \) is the adiabatic exponent, \( \rho_0 \) is the true density value of the material,
and $\langle \rangle_i$ indicates that the approximated value by using physical model at the position
of particle $i$. Considering the balance of the time step and the volume conservation of
the compressible fluid, there must exist an optimal value for $c$. The sound speed $c$
should be small enough, so that the time step can be increased to an acceptable value for
actual calculations. According to Monaghan (1994), $c$ is closely related to the bulk
velocity of the flow; that is, $c = \frac{|u_m|}{Ma}$, where $u_m$ is the maximum fluid bulk velocity,
and $Ma$ is the Mach number. To verify the weak compressibility hypothesis (when
$Ma = 0.01$ is assumed), $c$ must be at least 10 times higher than $u_m$ (Grenier et al.,
2013). Therefore, we set $c = 12.24$ m/s.

2.4. Interparticle potential force model simply combined with the Fowkes hypothesis

In SPH method, it is straightforward to include surface tension models, either
using the CSF model or the inter particle interaction force model. It can be said,
however, that only the Inter-Particle Force (IPF) model is practical in a system in which
three or more interfaces are dispersed. As in the Molecular Dynamics method, the
behavior of the fluid–fluid and fluid–fluid–solid interfaces in the IPF-SPH model results
from a force balance between pairwise interaction forces. Tartakovsky and Panchenko
(2016) developed a pairwise SPH formulation and derived the relationship between the
parameters in IPF and the surface tension and static contact angle. Their approximation
is similar to the SPH approximation of spatial derivatives. Kondo et al. (2007) proposed
simple IPF model based on the definition that surface tension can be considered as the
macro performance of an intermolecular force. Considering the interfacial force $F_s$, the
relationship between the interparticle force and interfacial energy has been clarified
theoretically, i.e. the interparticle potential is defined as $E(|r_{ij}|) = \frac{1}{3} (|r_{ij}| - \frac{3}{2} |r_{ij}|_0 + h_s) (|r_{ij}| - 2h_s)^2$; smoothing length for interfacial tension $h_s = 2.1 |r_{ij}|_0$ (Liu et al.,
2019). The interparticle potential force is defined using the space derivative of $E(|r_{ij}|)$.
$F_s$ is localized on the liquid interface by applying it to the liquid elements in the
transition region of the interface; the force per unit volume $\langle F_s \rangle_i$ is then converted into
a force per unit volume using the relation:

$$\langle F_s \rangle_i = -2\sigma_i |r_{ij}|_0^2 \left( \sum_{j=1}^{N} E(|r_{ij}|) \right)^{-1} \sum_{j=1}^{N} \frac{\partial E(|r_{ij}|)}{\partial r} \frac{r_{ij}}{|r_{ij}|}$$  \hfill (15)

where $\sigma_i$ is the interfacial tension, and $E$ is the interparticle potential. Free surfaces
are generally not smooth, dispersed phase often appeared. In VOF method, it is required
a considerably refined mesh to reproduce all the small-scale droplets normally with
diameter in a wide range, or must ignore them (Li et al., 2016). One of the merits of the
fully-Lagrange method is that it is possible to trace the disperse phase and the
continuous phase with the same scheme. Even when N=1 in eq. (15), the interfacial tension can be given by like pairwise force. This model can be simply expanded to calculate the multiphase interfacial force on the boundary, considering the Fowkes hypothesis (Fowkes, 1964). The Fowkes hypothesis explains that in a system in which two immiscible liquids (1 and 2) are in contact, the elements present at the two-phase interface are subject to forces, as shown in Fig. 1. On the interface, liquid 1 receives the attractive force $\sigma_1$ equivalent to the “surface tension” of liquid 1 and the dispersion force $\sigma_D$ from liquid 2. The difference between the attractive forces is the force $\sigma_1'$ acting on one liquid phase particle at the interface, defined in Eq. (16). The force $\sigma_2'$ acting on the interface particles of liquid 2 can be described similarly, as in Eq. (17).

\[
\sigma_1' = \sigma_1 - \sigma_D, \tag{16}
\]

\[
\sigma_2' = \sigma_D - \sigma_2. \tag{17}
\]

The difference between $\sigma_1'$ and $\sigma_2'$ denotes the interfacial tension $\sigma_{12}$ [Eq. (18)].

\[
\sigma_{12} = \sigma_1' - \sigma_2' = \sigma_1 + \sigma_2 - 2\sigma_D \tag{18}
\]

This simple hypothesis indicates that the unknown dispersion force and interfacial tension can be calculated explicitly using the surface tension as the input and the interfacial tension of the two liquids in contact as the conditions.

An example of two immiscible droplets contacting on a solid plate is
considered, as shown in Fig. 2. In terms of the tension balance on the solid–gas–liquid triple line in which liquid 1, the solid, and gas are in contact, the surface tension \( \sigma_1 \) of the liquid phase, surface tension \( \sigma_3 \) of the solid phase, and solid–liquid interfacial tension \( \sigma_{31} \) are considered to be balanced; in other words, Young's equation reflects a horizontal balance among the interfacial tensions:

\[
\sigma_1 \cos \theta_{31} + \sigma_{31} = \sigma_3, \tag{19}
\]

where \( \theta_{31} \) is the contact angle between liquid 1 and the solid plate. Here, the unknown solid surface tension and solid–liquid interfacial tension are eliminated from Young's equation and Fowkes' equation to obtain the following equation:

\[
\cos \theta_{31} = 2 \frac{\sigma_D}{\sigma_1} - 1. \tag{20}
\]

This equation indicates that the solid–liquid contact angle \( \theta_{31} \) is determined by the surface tension of the liquid phase and the dispersion force between the different phases. The dispersion force is explicitly defined by this equation, and the static contact angle can be calculated using the interparticle potential model. Furthermore, we similarly consider other triple lines, that among liquid 2, the solid and gas, and that among the two liquids and the solid, the Young's equation for which can be written as Eqs. (21) and (22), respectively.

\[
\sigma_2 \cos \theta_{23} + \sigma_{23} = \sigma_3, \tag{21}
\]
Here, $\theta_{23}$ is the contact angle between liquid 2 and the solid plate, and $\theta_{12}$ is the contact angle between the two liquids and the solid plate. Eliminating the terms pertaining to the unknown solid surface tension $\sigma_3$ and solid–liquid interfacial tension $\sigma_{31}$ and $\sigma_{23}$ from Eq. (19), (20) and (21), the following equation is obtained.

\[ \cos \theta_{12} = \frac{\sigma_1}{\sigma_{12}} \cos \theta_{31} - \frac{\sigma_2}{\sigma_{12}} \cos \theta_{23} \]  \tag{23}

This indicates that the solid–liquid contact angle $\theta_{12}$ is given by the contact angle $\theta_{31}$ and $\theta_{23}$. The variation of $\theta_{12}$ with the values of $\theta_{31}$ and $\theta_{23}$ is shown in Fig. 3, which presents the contact angle mapping for $\theta_{12}$ using typical interfacial tension values of matte and slag. Using this figure, it is possible to predict the wetting behavior when two immiscible liquids on a solid plate contact each other. When $\theta_{12}$ is 0°, liquid 2 mounts liquid 1 such that it has no contact with the solid phase, and the opposite behavior is noted when $\theta_{12}$ is 180°, with liquid 1 mounting liquid 2. The comparison with the analytical solution is in the Appendix. All programs are author’s original. Each computer code was written in Fortran90, and it was compiled and executed by Intel Fortran composer.

3. Analysis of binary droplet deformation
This section describes the SPH simulation for the deformation of two droplets that are initially stationary after they contact under $g = 0 \text{ m/s}^2$. The simulation was performed to verify the proposed model in the context of the equilibrium morphology based on comparison with the analytical solution. Further, we investigated the oscillation characteristics of a binary droplet.

### 3.1. Two liquids with identical physical properties

#### 3.1.1. Calculation conditions

Figure 4 shows the initial placement of two immiscible liquids. The identical physical properties of the liquid phase were assumed to correspond to the molten copper sulfide (matte) phase at 1573 K, as follows: surface tension $\sigma_1 = \sigma_2 = 0.4 \text{ N/m}$, density $\rho_1 = \rho_2 = 4,500 \text{ kg/m}^3$, viscosity $\mu_1 = \mu_2 = 3.13 \times 10^{-3} \text{ Pa\cdot s}$. Only the interfacial tension between the two liquids, $\sigma_{12}$, was varied from 0.2 to 1.0 N/m. A droplet was composed of 19,430 particles, with $|r_{ij}|_0 = 0.06 \text{ mm}$, and the time step $\Delta t = 1.0 \times 10^{-6} \text{ s}$.

#### 3.1.2. Results

Figure 5 shows the side view of droplet deformation for $\sigma_{12} = 0.2 \text{ N/m}$. All calculations were performed in three dimensions. The two liquids attracted each other
due to the interfacial tension, and exhibited an equilibrium shape after oscillation, which
is axially symmetric because of isotropic surface and interfacial tension. Figure 6
shows the side view in the equilibrium shape of the binary droplet at each interfacial
tension condition. As $\sigma_{12}$ increased, the contact area of the two liquids decreased
notably and the distance between the centers of gravity increased. According to the
Fowkes equation, given as Eq. (18), the attractive dispersion force $\sigma_d$ between the two
phases must decrease with increase in $\sigma_{12}$. Under the condition involving fixed $\sigma_1$ and
$\sigma_2$ (= 0.4 N/m), the stronger repulsion promotes the separation of the two phases. At
the liquid–liquid–gas triple line, $\sigma_1$, $\sigma_2$ and $\sigma_{12}$ are balanced on the basis of the
Neumann triangle; therefore, a triangle can be considered with sides of lengths $\sigma_1$, $\sigma_2$
and $\sigma_{12}$. The triangle inequality holds for this triangle, and the following relationship
holds on the triple line.

$$|\sigma_1 - \sigma_2| < \sigma_{12} < \sigma_1 + \sigma_2.$$  \hspace{1cm} (24)

When $\sigma_2 = \sigma_1$ in this system, Eq. (24) can be written as

$$0 < \sigma_{12} < 2\sigma_1.$$  \hspace{1cm} (25)

This relation indicates that the liquids separate completely if $\sigma_{12} > 2\sigma_1$. This condition
corresponds to $\sigma_{12} = 1.0$ N/m in Fig. 6, and it can be observed that the proposed
dynamic model predicted this analytical correlation accurately.
3.1.3. Effect of interfacial tension on the oscillation characteristics

Let the centers of gravity of the two liquids be $G_1$ and $G_2$. Figure 7 shows the time change of the distance between $G_1$ and $G_2$, $G_1G_2$, at each value of $\sigma_{12}$. Here, $G_1G_2$ was normalized using the initial radius of the droplet. Under all conditions, $G_1G_2$ exhibited damped oscillations. At $t = 0.1 \text{s}$, $G_1G_2$ increased with increase in $\sigma_{12}$, because the interface area between the two liquids decreased, as mentioned above.

Figure 8 shows the oscillation period of the droplets. Here, the oscillation period was defined as the time difference between the minimum and the maximum value of $G_1G_2$ after the droplet oscillated three times. The periods can be noted to be a downward trend when $\sigma_{12} \leq 0.3 \text{ N/m}$, but they exhibit an increasing tendency at $\sigma_{12} > 0.3 \text{ N/m}$. This indicates that as $\sigma_{12}$ increases, the surface tension acting on the free surface in each liquid becomes dominant instead of the attractive force acting on the two-liquid interface. In terms of the oscillation damping, as can be seen in Fig. 7, the two liquids in contact oscillated with decrease in the amplitudes due to viscous force while maintaining a constant oscillation period. Each damping rate of contacting droplets oscillation was shown in Fig. 9. Here, the difference between the minimum and maximum values of the curve decreased monotonously with time during the damping, and the rate of decrease was divided by the half period to calculate the damping rate.
The lower values of curves indicates that the oscillation damping was weak. Therefore, as $\sigma_{12}$ increased from 0.1 to 0.3 N/m, the oscillation damping became faster, and at 0.4 N/m, the damping rate was the almost same as that at 0.3 N/m despite the fixed viscosities $\mu_1$ and $\mu_2$. The damping became slower as $\sigma_{12}$ increased to 0.8 N/m. Under these conditions, the rate of oscillation damping was the highest at $\sigma_{12} = 0.4$ N/m.

During droplet oscillation, the liquids come in contact to form a two-phase interface; the interface area $A$ increases owing to the liquids attracting each other, and the interfacial energy $F = \sigma_{12} \cdot A$ increases (Natsui et al., 2017; 2020a). Then, the droplets start to move in opposite directions to reduce the excess energy at the equilibrium state, and the interface area decreases. Subsequently, the interface area increases again due to the amount deviated from the energy at equilibrium. After, this deformation is repeated, and an equilibrium shape is obtained via viscous damping. With regard to the oscillation period and viscous damping, a smaller interfacial tension corresponds to a smaller restoring force for the oscillation due to the formation of the interface. Specifically, with a small interfacial tension, the oscillation is dominated by the surface tension acting on the free surface of the droplet, whereas in case a large interfacial tension exists between two liquids, sympathetic oscillation due to the surface tension and interfacial tension
becomes apparent. For an interfacial tension of 0.3 N/m or more, the contribution of the interfacial tension to oscillation increases, and the tendency of the two liquids to separate increases; consequently, and the oscillation period is elongated.

3.2. Case study for actual matte-slag system

In this section, the interfacial behavior of an actual molten copper sulfide matte–molten slag system is considered. We assumed the physical properties of liquid 1 and 2 to correspond to matte and slag, respectively. The physical properties of matte phase was same as section 3.1, for the slag phase, $\sigma_2 = 0.2$ N/m, $\rho_2 = 3,500$ kg/m$^3$, and $\mu_2 = 0.10$ Pa·s. Here, density ratio $\rho_1/\rho_2 = 1.2$, viscosity ratio $\mu_2/\mu_1 = 32$. The initial placement of liquids is the same as that described in section 3.1. The time change of the shape of the liquids is shown in Fig. 10 ($\sigma_{12} = 0.1$ N/m). In Fig. 10, each vertical cross section was shown to help understanding of the interface shape inside the binary droplet. The asymmetry of the binary droplet is caused by the difference in each surface tension. According to the following well-known Young–Laplace equation, as:

$$\Delta P = \frac{2\sigma}{R},$$

where $\Delta P$ represents the pressure difference across the free surface, and $R$ represents the curvature radius of the droplet. Because the surface tension of liquid 1, $\sigma_1$, exceeds
\( \sigma_2 \), the pressure inside liquid 1 becomes larger than that inside liquid 2; consequently, the interfacial morphology between the two phases exhibits a positive curvature on the liquid 2 side, and a lens shape is observed in static state. Figure 11 shows the determined equilibrium shape at the range of \( \sigma_{12} = 0.1 \) to \( 0.6 \) N/m. In the case of a large \( \sigma_{12} \), liquids 1 and 2 exhibit a more spherical shape due to a reduction in the attractive force, owing to which the interface area decreases, and \( G_1G_2 \) increases. This aspect reflects that a large interfacial tension promotes the separation of the two phases.

Figure 12 shows the schematic diagram of the contact shape of the liquids. In Fig. 12(a), the triple line can be considered at the gas–liquid–liquid contact. At this triple line, the sum of the interfacial forces \( \sigma_1 \), \( \sigma_2 \), and \( \sigma_{12} \) must be zero in equilibrium state, according to the Neumann triangle. The tension sum can be calculated using scalar values, by considering a parallel line to rotation axis. Consider the following equation:

\[
\sigma_1 \cos \theta_1 - \sigma_2 \cos \theta_2 - \sigma_{12} \cos \theta_{12} = 0, \tag{27}
\]

where \( \theta \) represents the angle formed by the tension vector with respect to the rotation axis, as shown in Fig. 12(b). Here, \( \theta_1 \) and \( \theta_2 \) can be determined according to the obtained equilibrium shape. The left-hand side of Eq. (27) should ideally be zero; numerical errors, however, are likely to exist. The value on the left-hand side calculated is divided by \( \sigma_1 \), and the normalized value is defined as an error, the value of which are
listed in Table 1. Due to the numerical particle size of the fluid, SPH is not good at thin and wet liquid system. In Table 1, the error increased when $\sigma_{12}$ was smaller than 0.3 N/m due to the small angle formed by $\sigma_2$ and $\sigma_{12}$ as seen in the contact line in Fig. 11. When the interfacial tension is large, the contact line becomes ambiguous since liquid 1 has a spherical shape as shown in Fig. 11. In this measurement, since the contact line that was extrapolated from the liquid 2 surface outline was used, the error was thought to have increased due to the way the extrapolated line was made. The average error is approximately 10%, and the particle resolution affects the spatial resolution; this model, however, can express the balance of tension around triple lines.

**Figure 13** shows the time change of $G_1G_2$ under each tension condition. The binary droplet exhibited damped oscillations, and finally reached an equilibrium shape. With increase in $\sigma_{12}$, $G_1G_2$ increased at $t = 0.1$ s. As described in the previous section, as $\sigma_{12}$ decreased, the interfacial energy of the system, $F = \sigma_{12}A$, decreased as the interface area decreased, and thus, the two liquids separated and became spherical. **Figure 14** shows the oscillation period of the binary droplet under each interfacial tension. Under the considered conditions, the oscillation period became larger with increase in $\sigma_{12}$, likely due to the large interfacial tension that contributed to the separation of the two phases and increase in the amplitude of the oscillation, as
described in section 3.1. In addition, the viscosity of liquid 2 was approximately 32
times larger than that of liquid 1, which also contributed to the occurrence of rapid
oscillation damping. Figure 15 shows the damping rate of oscillation calculated in the
same manner as that shown in Fig. 9. The oscillation damping was more rapid for
\[ \sigma_{12} = 0.1 \text{ to } 0.4 \text{ N/m and slower for } \sigma_{12} \text{ ranging from } 0.4 \text{ to } 0.6 \text{ N/m.} \]
This tendency is almost similar to that exhibited under the condition of identical physical
properties, as described in section 3.1. The oscillation damping of the droplet can be
explained by the balance of \( \sigma_1, \sigma_2 \) and \( \sigma_{12} \), even when the density and viscosity of the
matte and slag are considered.

4. Binary droplet deformation on a flat solid surface

In pyrometallurgical processes, two immiscible liquids often come in contact
with the solid surface, and it is important to reveal their morphology and transient
behavior in the context of smelting reaction efficiency. In this section, we consider a
system in which one spherical liquid droplet with a diameter of 2 mm is placed on a
solid plate with a radius of 6 mm under gravity \( g = 9.8 \text{ m/s}^2 \). The hemispheres of the
droplet corresponded to liquids 1 and 2, as shown in Fig. 16.
4.1. Two liquids with identical physical properties

4.1.1. Calculation conditions

The identical physical properties of both the liquids were assumed to correspond to the molten copper sulfide matte, as considered in section 3.1. The contact angle between solid and liquid 1, \( \theta_{31} \), was set to a constant value of 90°, and only \( \theta_{23} \) was varied from 30° to 150°.

4.1.2. Results

Figure 17 shows the time change of the droplet shape on the plate at \( \theta_{23} = 60° \) and 120°. Figure 17 (a) and (c) show the cross-sectional views and (b) and (d) show the views from directly overhead for each \( \theta_{23} \) value. In the case of \( \theta_{23} = 60° \), liquid 2 wetted the flat plate under liquid 1 and reached the equilibrium shape. Although the density of both liquids was the same, \( \theta_{23} \) was smaller than \( \theta_{31} \) and liquid 2 wet the solid more easily than liquid 1 did. Therefore, liquid 1 rode on liquid 2. The transient shape of the droplet deformed to the lenslike shape observed at equilibrium. At \( \theta_{23} = 120° \), liquid 2 found it more difficult to spread on the solid surface than liquid 1 did, and thus, liquid 2 rode on liquid 1. Figure 18 shows the static shape for each value of \( \theta_{23} \). Here, the droplet shapes were compared at \( t = 0.032 \) s. Liquid 1 rode on liquid 2 at \( \theta_{23} = 30° \) and 60°; in contrast, liquid 2 rode on liquid 1 at \( \theta_{23} = 120° \) and 150°.
In the case of $\theta_{23} = 90^\circ$, liquids 1 and 2 were in half contact and the solid–liquid contact angle $\theta_{12}$ was $90^\circ$. As described in Eq. (23), the solid–liquid contact angle $\theta_{12}$ is governed by $\theta_{31}$ and $\theta_{23}$. The abovementioned results indicated that the solid–liquid triple line did not exist in the conditions of $\theta_{23} \leq 60^\circ$ or $\theta_{23} \geq 120^\circ$ and corresponded to the diagram of theoretical contact angles shown in Fig. 3 (a).

4.2. Case study the actual matte-slag binary droplet on solid surface

To investigate the actual matte–slag–solid system, the density and viscosity of liquid 2 were set as follows: $\rho_2 = 3,500 \text{ kg/m}^3$, and $\mu_2 = 1.00 \times 10^{-1} \text{ Pa}\cdot\text{s}$. The other conditions were the same as in section 4.1. Only $\theta_{12}$ was varied from $60^\circ$ to $120^\circ$. Figure 19 shows the time change of the shape of liquids at each $\theta_{23}$ value. Unlike the calculation described in section 4.1, it was empirically noted that the heavier liquid 1 pushed out liquid 2 on the slippery solid surface, and they exhibited large relative motion. At $\theta_{23} = 60^\circ$, when both liquids wet the solid plate, liquid 2 wrapped around liquid 1. The entire liquid phase moved slightly to the right of the plate with deformation and reached an equilibrium state. When $\theta_{23} = 90$ and $120^\circ$, liquid 2 rode on liquid 1, although liquid 1 remained hemispherical and liquid 1 encompassed liquid 2. The entire binary droplet moved to the right of the plate. Because the binary droplet
was initially arranged as a hemisphere, the droplet exhibited a sliding motion and deformed from the hemispherical shape to the equilibrium shape. It is considered that the distance of movement on the plate increased as the contact area to the solid phase decreased because a free-slip condition was assumed in this model. The theoretical solid–liquid contact angle $\theta_{12}$ under these calculation conditions is shown in the color contour diagram of Fig. 3 (b). According to the findings, the contact triple line of the solid and liquids 1 and 2 is stable only when $\theta_{23} = 90^\circ$, and it does not exist in the equilibrium shape pertaining to $\theta_{23} \leq 60^\circ$ or $\theta_{23} \geq 120^\circ$. Although these are theoretically expected contact states, both the liquids are stably contacted to the solid phase at $\theta_{23} = 60^\circ$. This difference can be explained by the density difference between liquids 1 and 2. When $\rho_1 > \rho_2$, liquid 1 pushes liquid 2 away due to gravity. Simultaneously, liquid 2 partially covers the free surface of liquid 1 because the surface tension of the liquid 2 is smaller than that of the liquid 1 such that the surface–interface energy of the system is reduced. In the case of $\theta_{23} = 90^\circ$, liquid 1 was completely covered by liquid 2, which was also a result of the smaller surface tension of liquid 2. The theoretical value of $\theta_{12}$ is $90^\circ$ in this case; thus, it can be understood that the two liquids are in contact with the solid phase correspondingly. In the case of $\theta_{23} = 120^\circ$, $\theta_{12} = 0^\circ$, and liquid 2 rode on liquid 1. Furthermore, in the system of $\theta_{23} = 90^\circ$, liquid
2 rode on liquid 1 and encompassed it.

Thus, it was noted that the balance of each interfacial tension, summarized as solid–liquid contact angles, contributed considerably to the change in the form of the two-liquid contact on the solid flat plate. The value of the solid–liquid contact angle was uniquely determined by the physical property of each liquid phase and the solid–liquid contact angle, although its value is not sufficient to predict the equilibrium contact morphology completely, i.e., the momentum due to the density difference between the two liquids should also be considered.

5. Conclusion

In this study, we established a model for interfacial tension between multiple phases for a three-dimensional SPH simulation scheme. The interparticle potential based approach was successfully expanded to a multi-interfacial tension model, considering the force balance between multiple phases including the free surface, in terms of the Fowkes theory.

We demonstrated the accuracy of the interfacial tension model by examining the equilibrium shape of a binary droplet with a free surface and comparing the results of the simulations with the analytical solutions. The validation was carried out for...
problems not involving gravity for binary droplet deformation under the surface–interfacial tension force. Satisfactory results that agreed with the theoretical considerations were attained. The oscillation characteristics of binary droplet could be determined via the balance of surface–interfacial tension even when the density and viscosity of the typical molten matte and slag were considered.

By further applying this model to a liquid–liquid–solid system including free surfaces, the temporal change in the shape of the binary droplet interface was demonstrated. Consequently, this model could estimate the transient behavior of the interfacial shape by considering the interfacial force balance. The oscillation characteristics of a binary droplet with a free surface were examined and a comparison between the results of the simulations and analytical solutions was performed. Furthermore, the model revealed that the contribution of gravity due to the density difference between the two liquids leads to a more complicated binary droplet morphology.

The proposed simplified multiple-fluid dynamic model can be applied in engineering problems because it requires the consideration of simple equations in contrast to the pairwise force model; furthermore, the model exhibits a high accuracy for interfacial shape prediction and has a low computational cost, owing to which it can
be used for problems such as those of large-scale dispersed phase flows. The proposed simulation framework can become a valuable tool for future implementations, for fluid flows involving more real phenomena such as the Marangoni effect, heat transfer, and chemical reaction between two liquids, and validations through comparisons between SPH simulations and experimental results.

Funding

This work was made possible by the financial support from the Grant-in-Aid for Scientific Research (KAKENHI grant no. 18K14036, 20H02491) of Japan Society for the Promotion of Science, the Network Joint Research Center for Materials and Devices (no. 20171106), the Iwatani Naoji Foundation (grant no. 16-4323), the Arai Science and Technology Foundation, the Iron and Steel Institute of Japan (ISIJ) Research Promotion Grant, and Steel Foundation for Environmental Protection Technology (SEPT). We would like to thank Editage (www.editage.com) for English language editing.
In this section, we verified the computational accuracy of proposed interfacial force model by comparing the numerical results with analytical/experimental results.

Theoretical solution exist for the oscillation mode and frequency under zero gravity. The simple and typical form which shows three-dimension has a cube. Lamb’s equation is known, where the oscillation period can be calculated by surface tension, droplet radius and liquid density. The vibration mode is axisymmetric oscillation of a droplet with a square cross section, and the equation expresses a period in which the long and short axes are interchanged. Accordingly, the oscillation period is given as \[ T = \frac{3}{\sqrt{72\sigma}} \cdot \frac{R^3}{\rho}, \]

where \( R \) represents the droplet radius, \( \rho \) represents the liquid density and \( \sigma \) represents the surface tension of the liquid. In analysis of droplet oscillation by the SPH, it is necessary to clarify the dependency between droplet oscillation and the sound speed \( c \), as the handling of the quasi-compressibility for spatial discretization using particles and similar factors are considered to influence local motion. Therefore, droplet motion was analyzed for various cases with different sound speed, and compared with analytically estimated oscillation period.

The droplet was arranged in a cubic shape with one side of 1 mm initially. The physical properties were as follows: surface tension \( \sigma_{\text{sur}} = 0.40 \text{ mN/m} \), density \( \rho = 4500 \)
kg/m$^3$, viscosity coefficient $\mu = 3.13 \times 10^{-3}$ Pa·s. As conditions in the numerical calculation, the particle diameter was 0.037 mm, the time step was $2.0 \times 10^{-7}$ s, and the number of the particles was 19683. In this calculation, the value of $c^2$ was changed to 60, 100, 150, 400, 600 m$^2$/s$^2$. Here, Larger $c$ makes higher pressure, and the liquid phase is less likely to be compressed.

The droplet deformed by the surface tension over time and reached the equilibrium shape. Figure A-1 shows the change of the droplet width $l$ over time when $c^2 = 150$ m$^2$/s$^2$. The width of the droplet oscillated with damping, and finally $l$ became a constant value. The oscillation period can be calculated by this result. Table A-1 shows the oscillation periods at each value of $c^2$. The oscillation period increases as $c$ increases, but $c$ does not greatly affect the oscillation period. This is because the mobility of the liquid particles decreases as the liquid phase tends to be uncompressed.

The radius of the equilibrium shaped droplet is 0.6204 mm, and the oscillation period $T$ can be calculated to be $1.21 \times 10^{-3}$ s with the density 4500 kg/m$^3$ and the surface tension 0.40 mN/m. This almost the same as the oscillation period calculated by SPH, especially when $c^2 = 150$ m$^2$/s$^2$. Based on this result, the surface tension can be calculated with this numerical model. We selected $c^2 = 150$ m$^2$/s$^2$ as the compressibility parameter in the text.
For liquid-liquid-solid contact, we observed the contact between water droplet and silicone oil droplet on a Teflon plate, and compared with the equilibrium shape obtained by SPH calculation. A water droplet with a volume of 20 μL was put on the plate, then a silicone oil droplet with 20 μL was put on the water droplet on the plate. The physical properties of water ($w$) and oil ($o$) are as follows: the surface tension $\sigma_w=72.8$ mN/m, $\sigma_o=20.1$ mN/m, the water-oil interfacial tension $\sigma_{wo}=52 \times 10^{-3}$ mN/m, the viscosity coefficient $\mu_w=1.5 \times 10^{-3}$ Pa·s, $\mu_o=9.35$ Pa·s, the contact angle to the Teflon surface $\theta_w=108.9$ deg, $\theta_o=16.4$ deg. Figure A-2 shows the water-oil contact morphology on the Teflon plate. As shown in experimental photograph, the oil covered the surface of the water phase which have a larger surface tension. Oil with a small contact angle spreads on the plate, and a water droplet exists in the center. The contact line of oil was affected by the surface state of the plate, and it became an distorted shape without spreading isotropically. An ambiguous outline of water droplet can be observed, but it is difficult to determine the exact outline of the water-oil interface because of the influence of the difference in refractive index between water and oil, and this must be solved in the future. According to the Eq. (23), the contact angle $\theta_{wo}$ when the water-oil-Teflon plate contacts can be calculated with the physical properties described above, and $\theta_{wo}$ is 145.5 deg. This indicates that there exists a water-oil-plate contact
angle, which implies that there is no oil layer between the water droplet and the plate, and the water droplet contacts with the plate directly. For Fig. A-2(a), the oil covered the surface of the water droplet, and outline of the whole droplet is in good agreement with the experiment. The water-oil interface, which was difficult to observe in the actual droplet, was shown in result, and water droplet was in contact with the plate. The water droplet did not spread on the substrate and became spherical. For Fig. A-2(b), the droplet was wet and spreaded isotropically because the surface of the plate was smooth, and the oil contact line became circular. Compared to the experiment, the radius of the contact line circle was smaller, and this depends on particle resolution, and it is considered that oil will spread thinly and widely if the number of the particles is ensured. The calculated contact angle was obtained from the equilibrium shape, and the water-oil-plate contact angle $\theta_A=147.3$ deg and the oil-plate contact angle $\theta_B=24.0$ deg. The given contact angles are 145.4 deg and 16.4 deg respectively, and the water-oil-plate contact angle well agrees with calculated value. For the contact line between the oil and the plate, smaller contact angle made the oil phase thinner. Therefore, it is considered that the size of the particles having a certain radius, and the contact angle was estimated to be larger.

As discribed above, the oscillation of a single droplet and the contact of
water-oil-plate were calculated, and it was verified that surface and interfacial tension
can be calculated with high accuracy in this SPH.
References


Fig. 1 Schematic of interfacial interaction between immiscible liquid phases (a) for interparticle potential model and (b) for Fowkes theory. $f$ in (a) denotes an attractive force.
Fig. 2 Depicted two contacting liquid droplets on a flat surface and these force balance.
Fig. 3 Contact angle value $\theta_{12}$ which is calculated by eq. 26. (a: $\sigma_1=0.4$ N/m, $\sigma_2=0.4$ N/m, $\sigma_3=0.1$ N/m, b: $\sigma_1=0.4$ N/m, $\sigma_2=0.2$ N/m, $\sigma_3=0.1$ N/m)
Fig. 4 Initial placement of two droplets.
Fig. 5 Time change of binary droplet morphologies at $\sigma_{12} = 0.2$ N/m.
Fig. 6 Equilibrium shape of binary droplet at each value of $\sigma_{12}$. 

$\sigma_{12} = 0.2 \text{ N/m}$  
$\sigma_{12} = 0.4 \text{ N/m}$  
$\sigma_{12} = 0.6 \text{ N/m}$  
$\sigma_{12} = 1.0 \text{ N/m}$
Fig. 7 Time change of the normalized $G_1 G_2$ by initial diameter of the droplet in each $\sigma_{ij}$ value.
Fig. 8 Oscillation periods at each $\sigma_{12}$ value.
Fig. 9 Damping rate of contacting droplets oscillation at each interfacial tension value.
Fig. 10 Time change of binary droplet morphologies assumed to be matte and slag at $\sigma_{12} = 0.1$ N/m.
Fig. 11 The equilibrium shapes of contacting two droplets at each interfacial tension value.
Fig. 12 The schematic diagram of contacting two droplets.
Fig. 13 Time change of the normalized $G_1 G_2$ by initial diameter of the droplet assumed to be matte and slag at each $\sigma_{ij}$ value.
Fig. 14 Oscillation periods of contacting droplet at each case.
Fig. 15 Influence of $\sigma_{12}$ value on the damping rate of binary droplets oscillation.
Fig. 16 Initial placement for contacting two droplets on a flat plate.
Fig. 17 Time change of binary droplet morphology on a flat plate at $\theta_{23} = 60$ deg and $\theta_{23} = 120$ deg. The physical properties of droplets are identical. (a) Cross-sectional view at $\theta_{23} = 60$ deg, (b) top view at $\theta_{23} = 60$ deg, (c) cross-sectional view at $\theta_{23} = 120$ deg, (d) Top view at $\theta_{23} = 120$ deg.
Fig. 18 Snapshots of binary droplet on a flat plate at each $\theta_{23}$ condition ($t = 0.032$ s).
Fig. 19 Time change of binary droplet morphology on a flat disk at each $\theta_{23}$ value. The physical properties of droplets are assumed to be matte and slag. Each snapshot show the cross-sectional and top view at (a) $\theta_{23} = 60$ deg, (b) $\theta_{23} = 90$ deg, and (c) $\theta_{23} = 120$ deg.
FIG. A-1. Time change of the width of the droplet when $c^2$ is 150 m$^2$/s$^2$. 
FIG. A-2. Comparison of experimental photographs and calculated shape of static water-oil contact shape on Teflon plate. (a): horizontal view, and (b): top view.
Table.1 The calculated values of LHS of Eq. (27) divided by $\sigma_1$.

<table>
<thead>
<tr>
<th>$\sigma_{12}$, N/m</th>
<th>0.1</th>
<th>0.2</th>
<th>0.3</th>
<th>0.4</th>
<th>0.5</th>
<th>0.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>error, %</td>
<td>13.9</td>
<td>21.5</td>
<td>6.0</td>
<td>4.8</td>
<td>11.8</td>
<td>15.3</td>
</tr>
</tbody>
</table>
Table A-1. Calculated values of oscillation period at each sound speed.

<table>
<thead>
<tr>
<th>$c^2$, m²/s²</th>
<th>60</th>
<th>100</th>
<th>150</th>
<th>400</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$, 10⁻³ s</td>
<td>1.16</td>
<td>1.17</td>
<td>1.24</td>
<td>1.38</td>
<td>1.46</td>
</tr>
</tbody>
</table>