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ORIGINAL CONTRIBUTION

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Determination of interfacial tension by the retraction method of highly deformed drop

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Abstract The traditional retraction of the deformed drop method (DDRM) to determine the interfacial tension is reformulated to relax the limit the small deformation assumption. The kernel of the new formalism is the calculation of the velocity gradient on the vertex of the ellipsoidal drop. Two models were used for such calculations: the Jackson and Tucker model [J Rheol 47:659–682] and the Yu and Bousmina model [J Rheol 47:1011–1039]. The method can be used either in the retraction of shear deformed drop, or in the retraction of elongated drops produced by the breakup of a long thread. Comparison with experimental results of the literature showed that conversely to the classical DDRM, good accuracy is obtained when the new modeling for the determination of interfacial tension is used both under small and large deformations.

Keywords Interfacial tension · Drop deformation · Large deformation · Polymer blends · Interface

Introduction

The interfacial tension is a crucial property of multiphase liquid systems such as classical emulsions and polymer blends. It directly characterizes the interactions at the interface between the components of the mixture. Various techniques are available for the determination of interfacial tension. Xing et al. (2000) compared five experimental techniques for the determination of interfacial tension in polymer blends and showed that the retraction of deformed drop method (DDRM) is of high simplicity and efficiency. Such a method can be used in the retraction of pre-sheared drops (Luciani et al. 1997; Guido and Villone 1999) or for elongated drops produced by the breakup of a long thread (Mo et al. 2000). DDRM method is based on a fundamental assumption that the drop is slightly deformed and it adopts an ellipsoidal shape with the three semiaxes $L(t)$, $B(t)$, $W(t)$ and $L(t) \geq W(t) \geq B(t)$, where t denotes time.

The DDRM used by Luciani et al. (1997) is based on the small deformation (SD) theory of Taylor (1934) and Rallison (1984). The crucial quantity to be measured for the determination of interfacial tension, Γ, is the variation in time of the deformation parameter $D_1(t) = L(t) - B(t)/L(t) + B(t)$ during the retraction process of the deformed drop. According to the small deformation theory, the evolution of $D_1(t)$ during the drop retraction can be written as

$$D_1(t) = D_0 \exp(-f_1 t/\tau) \tag{1}$$

with

$$f_1 = \frac{40(p+1)}{(2p+3)(19p+16)}, \quad \tau = \frac{\eta_m R}{\Gamma} \tag{2}$$

where $p = \eta_d/\eta_m$ is the ratio between the viscosity of the drop, η_d, and the matrix, η_m, R is the radius of an equivalent sphere having the same volume as the deformed drop ($R^3 = LBW$). D_0 is the initial deformation of the drop. The determination of the interfacial tension by Eq. (1) comes from the slope of the plot ln $D_1(t)/D_0$ vs time, t. To use Eq. (1), Luciani et al. (1997) assumed that the drop shape is axisymmetric ($B = W$). However, such assumption is not inherent to the small deformation theory (Mo et al. 2000) and one can in principle measure the three axes of the drop during the retraction process. Nevertheless for very small deformation, the difference between B and W and the axisymmetric assumption remains valid within the range of experimental errors of the technique. However, when the droplet shape departs largely from sphericity, the axisymmetric assumption becomes invalid. This is crucial because during experiments it is very difficult to apply very small deformations and at the same time visualize the shape of the deformed drop. It is also not easy to decide experimentally whether the deformation is small or not.

Another DDRM method was suggested by Mo et al. (2000), who used of the model of Maffettone and Minale (MM) (Maffettone and Minale 1998). In the MM model, the retraction of the ellipsoidal drop can be written as (Mo et al. 2000)

$$D_2(t) = L^2(t) - B^2(t) = \left(L^2 - B^2\right)_0 \exp\left(-f_1 t/\tau\right) \tag{3}$$

The MM model was proved to be accurate only to the zeroth order of drop deformation (Yu and Bousmina 2003; Yu et al. 2003), which means that Eqs. (1) and (3) are equivalent in describing the drop retraction. This is not surprising since the parameters of the MM model (parameter f_1 for instance) were determined from the SD theory. Nevertheless, it was shown that Eq. (3) works better than Eq. (1) when the deformation of drop increases (Mo et al. 2000). However even the MM model is not able to describe the drop deformation and retraction when the drop is subjected to large deformations (Yu and Bousmina 2003). Under large deformation neither the plot of ln $D_1(t)$ nor that of ln $D_2(t)$ vary linearly with time.

In this paper, we propose a new method that relaxes the small deformation assumption. The results of the new technique will be compared both to some experimental results of the literature and to the predictions of the SD and MM models.

Theory and Method

We describe the ellipsoidal drop by a second rank tensor $\boldsymbol{G}$ (Wetzel and Tucker 2001; Jackson and Tucker 2003; Yu and Bousmina 2003). In the principal axes of the drop, $\boldsymbol{G}$ can be expressed as

$$\boldsymbol{G}(t) = \begin{pmatrix} 1/L^2(t) & 0 & 0 \\ 0 & 1/B^2(t) & 0 \\ 0 & 0 & 1/W^2(t) \end{pmatrix} \tag{4}$$

where L, B, and W are the three semi-axes of the ellipsoidal drop. The time evolution of $\boldsymbol{G}$ is given by (Wetzel and Tucker 2001)

$$\frac{DG_{ij}}{Dt} + L_{ki}G_{kj} + G_{ik}L_{kj} = 0 \tag{5}$$

where D/Dt is the material derivate and L_{ij} is the velocity gradient tensor taken at the surface of the drop. During the retraction of the drop, L_{ij} possesses only diagonal components and therefore, Eq. (5) can be reduced to

$$\frac{d\ln L(t)}{dt} = L_{11}(t) \tag{6}$$

Similar expressions can be obtained for $B(t)$ and $W(t)$. Since the retraction of the drop is driven by interfacial tension, Eq. (6) can be used to determine its value during the retraction process. We will show later that L_{ij} can expressed in the following form:

$$L_{ij}(t) = F'_{ij}(t)\Big/\tau \tag{7}$$

where τ is a characteristic time that is related to the interfacial tension ($\tau = \eta_m R/\Gamma$, R being the radius of the initial spherical droplet) and $F''_{ij}(t)$ is a given function of time. The expression of $F'_{ij}(t)$ depends on the model under consideration and will be given later for the two models (JT and YB models). Equation (6) can be integrated to obtain

$$\ln\frac{L(t)}{L_0} = \frac{1}{\tau}\int_0^t F'_{11}(t')dt' = \frac{F_{11}(t)}{\tau} \tag{8}$$

where L_0 is the initial length of the drop. The interfacial tension can then be determined from the slope of ln $L(t)/L_0$ vs $F_{11}(t)$. $B(t)$ and $W(t)$ are given by equations similar to Eq. (8) and can also be used to determine the interfacial tension. It is, however, preferable to use $L(t)$ instead of $B(t)$ and $W(t)$ since the variation of $L(t)$ is larger and therefore the experimental errors are less important than those obtained with the other axes.

Let us now derive the analytical expression for L_{ij} as a function $F_{ij}(t)$ and interfacial tension, Γ using two approaches. The first approach is the use of the YB model that gives an analytical expression of L_{ij} at the surface of the drop using the boundary integral formalism. In the YB model, the velocity gradient due to the interfacial tension is expressed as

$$\boldsymbol{L} = \boldsymbol{L}^\alpha + \boldsymbol{L}^\beta \tag{9}$$

where $\boldsymbol{L}^\alpha$ is given by

$$\boldsymbol{L}^\alpha = \bar{\boldsymbol{L}}^\alpha - tr\left(\bar{\boldsymbol{L}}^\alpha\right)\boldsymbol{P} \tag{10}$$

where $\boldsymbol{P}$ is a constant diagonal matrix and takes the form

$$P_{ij} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & \frac{1}{2} & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix} \quad \text{for} \quad p \geqslant 1 \quad \text{and}$$
$$P_{ij} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & \frac{3}{2} & 0 \\ 0 & 0 & \frac{1}{2} \end{pmatrix} \quad \text{for} \quad p < 1 \tag{11}$$

The components of the tensor $\boldsymbol{L}^\alpha$ are obtained from the velocity at the surface of the ellipsoid:

$$\bar{L}^\alpha_{11} = u'^\alpha_1([L,0,0])/\tau L, \quad \bar{L}^\alpha_{22} = u'^\alpha_2([0,B,0])/\tau B,$$
$$\bar{L}^\alpha_{33} = u'^\alpha_3([0,0,W])/\tau W \tag{12}$$

$u'^\alpha_i (i = 1,2,3)$ is calculated by the boundary integral equation:

$$u'^\alpha_i(\boldsymbol{x}) = \frac{R}{2\pi(p+1)}\int\limits_{S_y} \frac{\boldsymbol{r}\cdot[\boldsymbol{n}(\boldsymbol{x}) + \boldsymbol{n}(\boldsymbol{y})]}{r^3} \times \left\{1 - \frac{3[\boldsymbol{r}\cdot\boldsymbol{n}(\boldsymbol{x})][\boldsymbol{r}\cdot\boldsymbol{n}(\boldsymbol{y})]}{r^2}\right\} dS_y \tag{13}$$

L^β is related to L^α by

$$diag(L^\beta) = A^{-1} \cdot B \cdot diag(L^\alpha) \tag{14}$$

where *diag()* mean the vector composed by the diagonal elements of the tensor between parenthesis. The tensors A and B are function of the viscosity ratio and the semiaxes of ellipsoids (Yu and Bousmina 2003):

$$\mathbf{A} = 2\begin{pmatrix} 1+(p-1)S_{11} & (p-1)S_{12} & (p-1)S_{13} \\ (p-1)S_{21} & 1+(p-1)S_{22} & (p-1)S_{23} \\ (p-1)S_{31} & (p-1)S_{32} & 1+(p-1)S_{33} \end{pmatrix} \tag{15}$$

and

$$\mathbf{B} = (p-1)\begin{pmatrix} 1-2S_{11} & -2S_{12} & -2S_{13} \\ -2S_{21} & 1-2S_{22} & -2S_{23} \\ -2S_{31} & -2S_{32} & 1-2S_{33} \end{pmatrix} \tag{16}$$

where S_{ij} is the Eshelby tensor expressed with contracted notation (Eshelby 1957). Equation (12) shows that $\bar{L}^\alpha$ is proportional to the interfacial tension, Γ, and thus L^β is also proportional to Γ. Therefore, L is directly proportional to Γ, and can be expressed in the form of Eq. (7). $F'_{ij}(t)$ can be obtained by multiplying Eq. (9) with τ. $F_{11}(t)$ is calculated by numerical integration over time period $0 \backsim t$ by using Eqs. (9), (10), (11), (12), and (13).

Another approach is suggested by Jackson and Tucker (2003) (the JT model). According to their model, the velocity gradient due to the interface is a blend of the Eshelby model and the slender-body model:

$$L = \begin{cases} fL_{\text{Eshelby}} + (1-f)L_{\text{slender}} & p<0.1 \\ L_{\text{Eshelby}} & p\geqslant 0.1 \end{cases} \tag{17}$$

where f is a mixing parameter which depends on the dimensionless length L/R of the ellipsoidal drop (Jackson and Tucker 2003). L_{Eshelby} is calculated by

$$L_{\text{Eshelby}} = -\frac{2q}{\pi\tau}B : S : \bar{P} \tag{18}$$

with

$$\bar{P} = P - \frac{1}{3}tr(P)\delta,$$
$$P = diag\left[\frac{R}{B}E\left(1-\frac{B^2}{W^2}\right), \frac{R}{W}E\left(1-\frac{W^2}{L^2}\right), \frac{R}{L}E\left(1-\frac{L^2}{B^2}\right)\right] \tag{19}$$

where q is a function of the viscosity ratio (Jackson and Tucker 2003). B and S are fourth-order tensors which are functions of viscosity ratio and the three semiaxes of ellipsoid (Wetzel and Tucker 2001).

L_{slender} is calculated as follows in the absence of flow:

$$L_{\text{slender}} = -\frac{\sqrt{L/R}}{2\sqrt{5}\tau\left(1+0.8p(L/R)^3\right)}\begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{bmatrix} + \frac{4}{3\tau(1+p)r_0/R}\left(1-\frac{r_0}{W}\right)\begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \tag{20}$$

Since L_{Eshelby} and L_{slender} are proportional to $1/\tau$, Eq. (17) can then be written in the form of Eq. (7). $F'_{ij}(t')$ for the JT model can be written as

$$F'_{ij}(t') = -f\frac{2q}{\pi}B(t') : S(t') : \bar{P}(t') + (1-f) \times \left\{ -\frac{\sqrt{L(t')/R}}{2\sqrt{5}\left(1+0.8p(L(t')/R)^3\right)} \times \begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & 0 \\ 0 & 0 & -\frac{1}{2} \end{bmatrix} + \frac{4}{3(1+p)r_0/R}\left(1-\frac{r_0}{W(t')}\right) \times \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \right\} \tag{21}$$

To sum-up, in both YB and JT models, the velocity gradient tensor can be expressed in the form of Eq. (7) and therefore the interfacial tension can be calculated from the slope of the plot ln $L(t)/L_0$ vs $F_{11}(t)$ (see Eq. 8). $F_{11}(t)$ is related to the function $F'_{11}(t')$ through (Eq. 8). The expression of $F'_{11}(t')$ is given explicitly for the JT model (Eq. 21). For the YB model, $F'_{11}(t')$ is given implicitly by Eqs. (9), (10), (11), (12), (13), and (14). In fact both L^α and L^β (L^β is related to L^α by Eq. 14) can be written if the form given by Eq. (12), where the velocity has to be integrated numerically at the apex of the ellipsoid. This means that the velocity gradient given by Eq. (9) can also be expressed in the form given by Eq. (12) and therefore by Eq. (7) that has to be used to extract the interfacial tension from the characteristic time $\tau = \eta_m R/\Gamma$.

To use the method more simply, an approximate procedure is suggested in the Appendix. The values of the function $F'_{11}(t)$ appearing in Eq. (8) can be directly calculated from the values supplied in Table A1.

Results and discussions

It has been shown that the YB and the JT models can describe the deformation and relaxation of the drop in a quite satisfied manner (Jackson and Tucker 2003; Yu and Bousmina 2003), including the case of large deformation. Hence, the determination of interfacial tension by drop retraction from YB model or JT model relaxes the restriction about the small deformation assumption. We thus examined this approach for systems with various viscosity ratios and various initial deformations of the drop. The interfacial tension obtained from the new approach is compared to that determined experimentally using the small deformation models.

When the initial deformation of the drop is very large, neither the deformation parameter D nor the parameter L^2–B^2 can be described by a single exponential decrease like Eqs. (1) or (3). This is shown more explicitly in Fig. 1, where the scatter symbols represent the experimental data of Almusallam et al. (2000) for PBd/PDMS system with $p = 1$ and the strain of pre-shear $\gamma_0 = 5.0$, and the solid lines represent the predictions obtained from Eqs (1) and (3). Clearly, the small deformation models are unable to describe the relaxation of the drop after imposition and cessation of a large amplitude of deformation. One can argue that the fit can be carried out at longer times in the linear region. This of course gives better results for the determination of interfacial tension by the SD models, but the linear zone is not always well identified when the drop is deformed under large amplitude of deformation. Of course, if the technique has to be used for viscoelastic components, it is better to consider a time interval starting beyond the longer time of elastic relaxation of the pure components, where the drop shape recovery is only driven by interfacial tension. Examination of various systems revealed in fact that even in this case the variation of the deformation parameter in time (Eqs. 1 and 3) is not clearly linear.

The calculations of the interfacial tension based on YB and JT models are shown in Fig. 2, which illustrates excellent agreement between the experiments and the models fit. The interfacial tension determined by YB and JT models are 1.9 mN/m and 2.4 mN/m respectively.

In Table 1, we compare the calculation results by different methods for different systems. χ^2 in the table denotes the correlation coefficient of the linear fit. It is shown that SD and MM models give acceptable results only for very small deformation (Nos. 1, 5, 6), i.e., the maximum stretch ratio is of about 3. MM model seems to do a better job than SD model due to its good linear fit with experiments. The new approach gives better linear fit with the experimental data for the retraction of slightly deformed drop than the traditional DDRM, and thus the determined interfacial tension is slightly larger than the traditional methods. However, the difference between the interfacial tension measured by the traditional method and the new approach lies within the acceptable experimental errors. The advantages of the new approach become significant when the initial deformation of drop is large. It is seen from Table 1 that SD and MM models fail to fit the experimental results for large drop deformation (Nos. 2–4 and 7–8), while YB and the JT models can still fit the experimental results quite well (except No. 8).

It is also noticed that the interfacial tension determined by YB model starts to decrease when the stretch ratio L_0/B_0 of drop is larger than 10. This might be due to the over-simplified determination of the velocity gradient tensor by Eq. (11). The interfacial tension determined by JT model for PIB/PDMS system is larger than all other models. This is probably because the viscosity ratio ($p = 0.0667$) is near the transition zone between the Eshelby result and the slender-body result in the JT model.

The new approach can be applied to drop retraction after imposition of both small and large deformations. One restriction of this method is that the shape of the drop should remain ellipsoidal. This condition is satisfied under most cases except for systems with very small viscosity ratio and large initial deformation (No. 8). When $p \ll 1$ and $L_0/B_0 \gg 1$, the shape of the drop changes into rod or dumbbell during the retraction. For systems with $p \ll 1$, it is better to measure the interfacial tension by the drop retraction with limited initial drop deformation ($L_0/B_0 < 10$).

Another approach for the determination of interfacial tension for largely deformed drop has been suggested by Tjahjadi et al. (1992). The technique is also available for shapes other than ellipsoid. However, the Tjahjadi et al. (1992) technique is based on a large number of previous numerical simulations by using boundary integral method and the determination of the interfacial tension was obtained with some curve-fittings and interpolations from their tabulated results. Moreover, the results of these add-hoc curve fittings provide values of interfacial tension only for p = 0.01~10. If the technique has to be applied to viscosity ratio other than

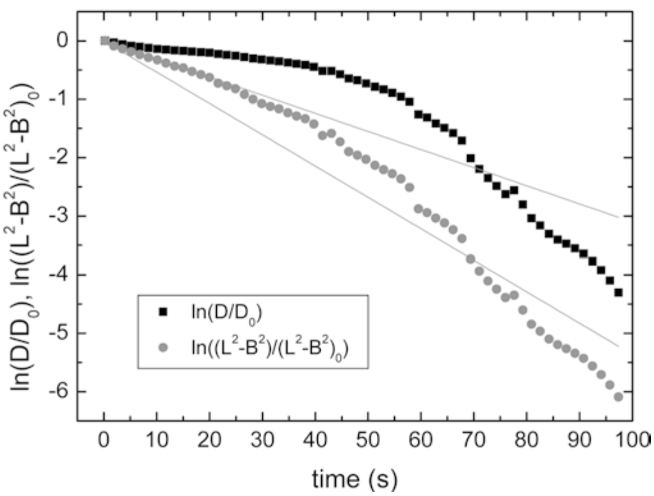

Fig. 1 Determination of the interfacial tension by the SD model and the MM model

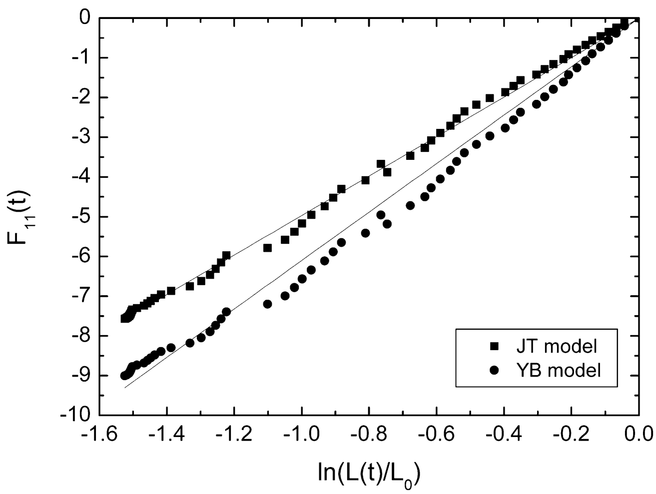

Fig. 2 Determination of the interfacial tension by JT model and YB model

Table 1 Comparisons of different methods in different systems

No.	System	References	Viscosity ratio	$\frac{L_0}{B_0}$	Eq. (1)		Eq. (3)		Eq. (8)			
					SD model		MM model		YB model		JT model	
					Γ (mN/m)	χ^2	Γ (mN/m)	χ^2	Γ (mN/m)	χ^2	Γ (mN/m)	χ^2
1	PBd/PDMS	Almusallam et al. (2000)	1.0	1.4	2.0	0.947	2.4	0.980	2.6	0.997	2.8	0.998
2	PBd/PDMS	Almusallam et al. (2000)	1.0	7.4	1.3	0.936	1.9	0.985	2.3	0.999	2.5	0.999
3	PBd/PDMS	Almusallam et al. (2000)	1.0	12.4	0.73	0.857	1.2	0.957	1.6	0.992	1.8	0.998
4	PBd/PDMS	Almusallam et al. (2000)	1.0	18.8	0.79	0.780	1.4	0.929	1.9	0.988	2.4	0.997
5	PMMA/PS	Mo et al. (2000)	2.14	2.2	0.49	0.966	0.62	0.995	0.61	0.999	0.65	0.999
6	PIB/PDMS	Yamane et al. (1998)	0.0667	2.9	2.6	0.990	3.0	0.994	3.2	0.992	3.6	0.989
7	PIB/PDMS	Yamane et al. (1998)	0.0667	11.0	1.2	0.850	1.9	0.950	2.4	0.986	3.7	0.998
8	PIB/PDMS	Yamane et al. (1998)	0.0667	44.2	0.4	0.445	0.9	0.811	1.0	0.945	2.4	0.972

this range, further numerical simulations and curve fittings have to be performed.

The approach proposed in the present paper does not require any curve fittings and can be applied to arbitrary viscosity ratio both under small and large deformations.

Conclusions

The traditional DDRM to determine the interfacial tension by SD model or MM model is updated with extension to large drop initial deformation by using YB model or JT model. This approach requires accurate measurement of the length of three axes during the drop retraction. The method shows good description of the experimental results and thus the error on the determination of interfacial tension is very small compared to the classical DDRM method that fails when the drop is deformed under large amplitude of deformation.

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Appendix

To make easy use of the method proposed is the present paper we provide here an approximate method for the function $F'_{11}(t)$ appearing in the YB model for various viscosity ratios and various aspect ratios. The function $F'_{11}(t)$ can be fitted using the following polynomials:

$$F'_{11}(t) = \frac{\sum_{j=1}^{n}\sum_{i=1}^{m} k_{ij}c^{i-1}(t)d^{j-1}(t)}{L(t)} \tag{A1}$$

where $c(t) = B(t)/L(t)$ and $\mathrm{d}(t) = B(t)/W(t)$ are two aspect ratios. The coefficients k_{ij} for a given range of viscosity ratio, p, are listed in Table A1. $F_{11}(t)$ can be easily calculated from Eq. (8) together with Eq. (A1). For other values of p not listed in the table, a linear interpolation can be made from $F_{11}(t)$ between the nearest values of p. The coefficients for p out of the range 0.01∼10 are not listed in Table A1. Direct calculation using the model is recommended for these viscosity ratios.

The fitting procedure used here is somewhat similar to the one adopted by Tjahjadi et al. (1992). The estimation of interfacial tension from their method needs first the knowledge of a theoretical curve $L(t)/R \backsim t$, which is determined by double linear interpolations from the fitting results of numerical simulations. Then interfacial tension is determined by taking two shapes during retraction for the aspect ratios and non-dimensional time from the curve $L(t)/R \backsim t$. The advantage of the method suggested by Tjahjadi et al. is its ability to describe some complex shapes, such as dumbbell and other non-ellipsoidal shapes. However, there are two concerns about such a method. (i) If the viscosity ratio and the initial aspect ratio is not included in the table of polynomial coefficients, which are fitted from the numerical simulations, double linear interpolations are needed. Additional assumptions had been made in such a procedure such that the evolution of aspect ratios is a bilinear function of viscosity ratio and the initial aspect ratio. In contrast, our approach only (implicitly) assumes that $F_{11}(t)$ is a linear function of viscosity ratio. (ii) Usually, only two shapes of the drop during the retraction are needed to determine the interfacial tension from the method suggested by Tjahjadi et al. (1992). Therefore, this poses the problem of the choice of the best images to be selected. The authors did not supply any information about this issue. If a series of two different images are used, it is then expected that one will obtain a series of interfacial tensions from the method. Such a problem is not encountered in our method. The interfacial tension is obtained only from the fitting of the straight line $F_{11}(t) \backsim \ln L(t)/L_0$. Therefore, there is no need to find the two best images or the way of making averages.

Table A1 Polynomial coefficients k_{ij} in Eq. (<equationcite>A1</equationcite>) for a range of viscosity ratio

k_{ij}	i	j					
		1	2	3	4	5	6
P = 0.01	1	−3.34737	−28.1724	157.7431	−291.89	238.5905	−73.935
	2	22.06498	267.2864	−1482.69	2766.35	−2289.83	718.9385
	3	−100.41	−973.284	5685.755	−10727.4	8925.924	−2813.87
	4	230.534	1688.293	−10471.4	19947.48	−16645.6	5255.892
	5	−251.452	−1354.4	9098.176	−17531	14673.03	−4638.92
	6	103.1022	399.8038	−2989.5	5841.522	−4906.74	1553.385
p = 0.02	1	−3.29325	−28.4503	158.2858	−292.38	238.7801	−73.954
	2	20.82154	273.9623	−1496.58	2780.364	−2296.61	720.1772
	3	−91.5875	−1018.76	5777.781	−10818.2	8969.236	−2821.74
	4	206.0459	1811.044	−10713	20178.6	−16751.8	5274.242
	5	−222.637	−1495.68	9369.255	−17782.4	14783.61	−4656.77
	6	91.10536	457.5474	−3097.86	5939.09	−4947.84	1559.525
p = 0.04	1	−3.40485	−27.7864	156.6999	−290.47	237.6155	−73.666
	2	23.60419	258.2936	−1461.29	2740.694	−2274.32	715.1606
	3	−109.759	−914.305	5540.574	−10551.1	8819.719	−2788.39
	4	253.3935	1537.139	−10089.4	19475.64	−16358.1	5186.477
	5	−274.505	−1195.43	8686.341	−17013.9	14354.13	−4561.2
	6	111.1412	341.6672	−2834.9	5644.09	−4783.54	1523.083
p = 0.06	1	−3.09774	−28.7796	158.1226	−291.677	238.1929	−73.7728
	2	16.27039	282.4386	−1497.89	2775.381	−2293.69	719.6427
	3	−58.1271	−1081.1	5786.136	−10777.9	8945.518	−2817.74
	4	107.9613	1998.168	−10745.2	20059.66	−16675.7	5260.064
	5	−98.8607	−1741.27	9433.712	−17651.7	14692.56	−4638.87
	6	35.22381	573.0056	−3139.41	5892.044	−4911.5	1552.159
p = 0.08	1	−3.10503	−28.6561	157.7095	−291.096	237.8061	−73.6711
	2	16.4856	279.967	−1490.91	2767.304	−2289.61	718.9221
	3	−58.2672	−1068.53	5743.702	−10725.3	8918.068	−2812.86
	4	104.9474	1977.637	−10650.3	19929.28	−16602.7	5246.074
	5	−91.2483	−1735.73	9354.558	−17524.3	14615.34	−4623.03
	6	30.47119	578.0796	−3119.69	5850.161	−4883.57	1546.05
p = 0.1	1	−3.22409	−28.4027	157.6854	−291.333	237.9298	−73.6679
	2	19.55258	273.5504	−1491.76	2777.711	−2297.47	720.5802
	3	−79.762	−1020.26	5739.008	−10785.5	8966.895	−2823.59
	4	166.9257	1829.289	−10604.1	20059.46	−16718.3	5271.687
	5	−168.481	−1540.83	9260.986	−17638.7	14731.76	−4649.09
	6	64.77712	487.8793	−3065.12	5883.788	−4925.41	1555.562
p = 0.2	1	−3.10395	−28.7115	157.6542	−290.503	236.9713	−73.3203
	2	17.36909	281.1456	−1502.32	2786.249	−2301.92	721.6972
	3	−62.9605	−1071.55	5799.84	−10829.8	8993.977	−2832.7
	4	118.5221	1967.799	−10745.2	20136.9	−16763.5	5290.042
	5	−109.21	−1706.44	9415.831	−17702.9	14763.81	−4665.04
	6	38.83065	560.0076	−3130.17	5905.914	−4934.04	1560.818
p = 0.4	1	−3.21902	−28.2231	156.3776	−288.281	234.9246	−72.5944
	2	21.47004	269.9021	−1493.85	2788.319	−2306.14	722.6327
	3	−87.8588	−994.353	5727.639	−10830.1	9026.09	−2844.61
	4	183.4334	1752.177	−10508.1	20071.83	−16808.3	5313.172
	5	−183.139	−1454.96	9121.348	−17588.7	14785.45	−4683.42
	6	69.16324	456.5177	−3006.62	5852.482	−4936.73	1566.34
p = 0.6	1	−3.06443	−29.0166	157.6868	−288.839	234.4612	−72.2454
	2	19.07738	289.2663	−1546.29	2854.607	−2346.01	731.8004
	3	−69.1201	−1125.01	6073.411	−11275.7	9307.673	−2914.54
	4	130.508	2095.164	−11391.8	21201.47	−17524.8	5493.324
	5	−122.117	−1834.85	10080.42	−18802.7	15552.98	−4876.68
	6	44.56038	605.6088	−3377.05	6317.22	−5229.3	1639.932
p = 0.8	1	−3.05308	−28.9198	156.776	−286.617	232.2467	−71.453
	2	20.11896	287.1201	−1544.74	2852.95	−2343	730.1129
	3	−74.346	−1109.31	6058.062	−11273.3	9310.11	−2914.67
	4	142.066	2048.135	−11321.5	21157.59	−17516.4	5493.773
	5	−133.311	−1780.47	9983.39	−18724.7	15526.64	−4874.24
	6	48.39807	584.5126	−3335.51	6280.026	−5214.67	1638.08

Table A1 (Contd.)

k_{ij}	i	j 1	2	3	4	5	6
p = 1	1	−1.25472	3.41074	−6.65438	6.23705	−2.25199	0
	2	6.87437	−30.611	66.45333	−67.2988	25.42357	0
	3	−24.0241	122.0643	−268.549	273.9439	−104.22	0
	4	48.87458	−239.774	513.4792	−518.378	196.8722	0
	5	−49.3869	227.3271	−465.716	460.6496	−173.781	0
	6	19.1027	−82.7048	161.2039	−155.322	58.00922	0
p = 1.3	1	−1.20992	3.15701	−6.08928	5.6577	−2.03046	0
	2	6.58602	−27.9623	59.55491	−59.4854	22.23098	0
	3	−21.0503	108.949	−242.124	246.63	−93.2232	0
	4	38.5418	−205.477	459.9598	−471.394	179.1774	0
	5	−36.0346	187.7904	−413.821	421.7984	−160.292	0
	6	13.26633	−66.577	142.6669	−143.409	54.21306	0
p = 1.7	1	−1.1869	2.97954	−5.66908	5.23105	−1.87257	0
	2	6.97393	−27.5435	56.48925	−55.3445	20.47911	0
	3	−22.4132	108.0543	−231.181	230.7424	−86.2157	0
	4	40.06518	−203.406	440.8747	−443.263	166.4851	0
	5	−36.304	184.2819	−396.566	397.6835	−149.43	0
	6	12.96318	−64.5008	136.2077	−135.235	50.62092	0
p = 2.0	1	−1.16186	2.80989	−5.28877	4.85926	−1.73873	0
	2	7.0329	−26.2004	52.4952	−51.0061	18.83302	0
	3	−22.0973	100.6385	−211.179	209.8942	−78.4724	0
	4	37.70025	−183.496	393.7078	−396.87	149.815	0
	5	−32.3831	160.0978	−344.844	349.5909	−132.757	0
	6	10.99309	−53.9444	115.2006	−116.602	44.37213	0
p = 2.3	1	−1.14721	2.69192	−5.00214	4.56182	−1.62682	0
	2	7.32112	−26.0193	50.66197	−48.4327	17.72479	0
	3	−23.6556	101.8642	−206.485	201.147	−74.3292	0
	4	40.98761	−188.753	389.8626	−383.92	142.8881	0
	5	−35.5165	166.8693	−345.48	341.2521	−127.483	0
	6	12.09423	−56.7601	116.5509	−114.745	42.8767	0
p = 2.7	1	−1.12226	2.5164	−4.59603	4.15142	−1.47487	0
	2	7.52753	−25.145	47.35823	−44.4867	16.13767	0
	3	−24.7737	99.5934	−194.489	185.764	−67.926	0
	4	43.08784	−185.896	369.6509	−356.505	131.142	0
	5	−37.2324	165.0666	−329.473	318.5959	−117.533	0
	6	12.58913	−56.2351	111.6552	−107.652	39.7036	0
p = 3.0	1	−1.11009	2.41577	−4.34536	3.8854	−1.37316	0
	2	7.80151	−25.0662	45.90192	−42.3341	15.18958	0
	3	−26.5469	101.8796	−192.159	179.2876	−64.5984	0
	4	47.34047	−194.589	371.9163	−348.767	125.9704	0
	5	−41.6752	176.1603	−336.961	315.6129	−113.958	0
	6	14.2642	−60.9032	115.7611	−107.819	38.81903	0
p = 3.3	1	−1.09067	2.28929	−4.05859	3.59656	−1.26599	0
	2	7.87698	−24.253	43.37786	−39.4674	14.05747	0
	3	−27.0916	99.37091	−182.652	167.8818	−59.9659	0
	4	48.48688	−190.908	355.4711	−328.103	117.3631	0
	5	−42.7162	173.6214	−323.78	298.3497	−106.594	0
	6	14.60697	−60.2274	111.7619	−102.391	36.45332	0
p = 4.0	1	−1.04994	2.02606	−3.45854	2.98739	−1.03855	0
	2	8.05383	−22.603	38.19021	−33.5226	11.69724	0
	3	−28.571	94.95871	−163.911	144.7479	−50.4617	0
	4	51.96966	−185.741	323.9985	−286.472	99.72621	0
	5	−46.1715	171.1314	−298.91	263.3175	−91.3464	0
	6	15.83841	−59.8827	104.2123	−91.1807	31.46539	0
p = 5.0	1	−0.98145	1.64147	−2.62823	2.17053	−0.73911	0
	2	7.83774	−18.9847	29.41431	−24.533	8.33867	0
	3	−27.8142	79.46272	−125.254	105.3115	−35.8155	0
	4	49.66089	−152.999	243.6802	−205.868	70.14278	0
	5	−42.9494	137.9964	−220.425	186.2927	−63.4952	0
	6	14.30144	−47.1979	75.28253	−63.4479	21.59445	0

Table A1 (Contd.)

k_{ij}	i	j					
		1	2	3	4	5	6
p = 7.0	1	−0.87472	1.07146	−1.41422	0.96653	−0.29316	0
	2	7.55617	−13.7305	16.93126	−11.5622	3.4139	0
	3	−27.9529	59.89721	−74.959	51.76951	−15.2437	0
	4	51.16538	−118.633	150.2679	−104.452	30.76598	0
	5	−45.0195	109.4468	−139.638	97.17768	−28.5717	0
	6	15.17737	−38.1267	48.87075	−33.9497	9.94392	0
p = 10.0	1	−0.74487	0.52211	−0.40879	0.08517	0	0
	2	6.82006	−7.83078	5.5869	−1.4093	0	0
	3	−25.8312	35.35634	−25.5181	6.86365	0	0
	4	47.69375	−71.1609	52.1025	−14.4603	0	0
	5	−41.9946	66.12285	−49.0716	13.8846	0	0
	6	14.09987	−23.0628	17.32902	−4.97159	0	0

References

Almusallam AS, Larson RG, Solomon MJ (2000) Constitutive model for the prediction of ellipsoidal droplet shapes and stresses in immiscible blends. J Rheol 44:1055–1083

Eshelby JD (1957) The determination of the elastic field of an ellipsoidal inclusion, and related problems. J Fluid Mech 44:65–78

Guido S, Villone M (1999) Measurement of interfacial tension by drop retraction analysis. J Colloid Interface Sci 209:247–250

Jackson NE, Tucker CL (2003) A model for large deformation of an ellipsoid droplet with interfacial tension. J Rheol 47:659–682

Luciani A, Champagne MF, Utracki LA (1997) Interfacial tension coefficient from the retraction of ellipsoidal drops. J Polym Sci B Polym Phys 35:1393–1403

Maffettone PL, Minale M (1998) Equation of change for ellipsoidal drops in viscous flow. J Non-Newtonian Fluid Mech 78:227–241

Mo H, Zhou CX, Yu W (2000) A new method to determine interfacial tension from the retraction of ellipsoidal drops. J Non-Newtonian Fluid Mech 91:221–232

Rallison JM (1984) The deformation of small viscous drops and bubbles in shear flows. Annu Rev Fluid Mech 16:45–66

Taylor GI (1934) The formation of emulsions in definable fields of flow. Proc R Soc A 146:501–523

Tjahjadi M, Stone HA, Ottino JM (1992) Satellite and subsatellite formation in capillary breakup. J Fluid Mech 243:297–317

Wetzel ED, Tucker CL (2001) Droplet deformation in dispersions with unequal viscosities and zero interfacial tension. J Fluid Mech 426:199–228

Xing P, Bousmina M, Rodrigue D, Kamal MR (2000) Critical experimental comparison between five techniques for the determination of interfacial tension in polymer blends: model system of polystyrene/polyamide-6. Macromolecules 33:8020–8033

Yamane H, Takahashi M, Hayashi R, Okamoto K, Hashihara H, Masuda T (1998) Observation of deformation and recovery of polyisobutylene droplet in a polyisobutylene/poly-dimethyl siloxane blend after application of step shear strain. J Rheol 42:567–580

Yu W, Bousmina M (2003) Ellipsoidal model for droplet deformation in Newtonian systems. J Rheol 47:1011–1039

Yu W, Bousmina M, Zhou CX (2003) Drop deformation in viscoelastic system: small deformation analysis. J Rheol (submitted)