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DROPLET INTERACTIONS IN THERMOCAPILLARY MOTION

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Abstract—The dynamics of two spherical droplets, whose movement is driven by variations in interfacial tension caused by a temperature gradient, are analyzed using a method of reflections. Both droplets have the same internal fluid properties but may differ in size, and the configuration of the droplets is arbitrary relative to the direction of the undisturbed temperature gradient. The method of reflections is based on an analysis of the thermal and hydrodynamic disturbances produced by a single droplet placed in an arbitrarily varying temperature field. The results for two-droplet interactions are correct to $0(r^{-6})$ where r is the center-to-center distance between the droplets. For the specific case of bubbles oriented parallel with the undisturbed temperature gradient, my results agree very well with numerical calculations found in the literature. The results for two, identical droplets are used to find the $0(\phi)$ effect on mean droplet velocity of a bounded suspension, where ϕ is the volume fraction of the droplets. In general, the interactions between droplets moving by thermocapillary effects are much weaker than in the case of sedimentation.

1. INTRODUCTION

Young *et al.* (1959) demonstrated mathematically and experimentally that gradients of interfacial tension can drive the motion of droplets suspended in a second fluid. The interfacial tension (γ) varies about the surface of the droplet because there exists a gradient of temperature (T) or chemical compositon (C) in the surrounding fluid. Assuming that γ decreases with increasing T, the droplet moves toward hotter regions because of the nonuniform stresses at its surface which tend to pull the surface from the hot side to the cold side. If the droplet is spherical with radius a, and if it is sufficiently small that convective contributions to heat and momentum transport are negligible, the droplet velocity is computed from the following expression which Young *et al.* derived:

$$\mathbf{U}^{(o)} = \frac{2}{(2+k^*)(2+3\eta^*)}\,\frac{a}{\eta}\left(-\frac{\partial\gamma}{\partial T}\right)\nabla T_\infty, \qquad [1]$$

where ∇T_∞ is the temperature gradient (assumed uniform) if the droplet were not there, η is the viscosity of the surrounding fluid, and k^* and η^* are the ratios of the thermal conductivities and viscosities, respectively, between internal and surrounding fluids. (Note that typographical errors occur in [9] of Young *et al.* (1959).) Equation [1] also holds for motion induced by gradients of composition, with C replacing T and KD^* replacing k^* where K is the solute distribution coefficient between internal and surrounding fluids and D^* is the ratio of solute diffusion coefficients.

Significant advances in the mathematical analysis of thermocapillary driven movement of droplets have been made by Subramanian and co-workers. The effects of convective heat transfer have been examined (Subramanian 1981, 1983) and found to be $0(\mathrm{Pe}^2)$ where Pe equals the Peclet number based on droplet radius, droplet velocity as calculated from [1], and thermal diffusivity of the surrounding fluid. Meyyappan *et al.* (1981) solved for the correction to [1] in the case where a bubble moves perpendicularly to an infinite planar surface and found the boundary effect to be relatively weak compared to that experienced by a sphere undergoing sedimentation. Meyyappan *et al.* (1983) solved the problem of two bubbles which are aligned with the undisturbed temperature gradient using an exact representation in bipolar coordinates, while Meyyappan & Subramanian (1984) obtained the velocity of two arbitrarily oriented bubbles, correct to $0(r^{-3})$ where r is the center-to-center spacing, using an approximate technique based on a single reflection of thermal and hydrodynamic disturbances caused by one of the bubbles. An important result of these latter two studies is that the interaction between two bubbles is asymptotically of $0(r^{-3})$, rather than $0(r^{-1})$ as for the interaction between two Stokeslets (Happel & Brenner 1973); hence, the correction to [1] in the case of two bubbles in proximity is relatively weak compared to configurational effects expected in sedimentation.

In this paper I derive the velocity of two spherical droplets as a function of their separation (r) and orientation ($\hat{\mathbf{e}} = \mathbf{r}/r$) relative to the undisturbed, constant gradient ∇T_∞. Reynolds numbers are assumed small so that the Stokes equations apply. A method of reflections is used to evaluate the effects of one droplet on the local velocity and temperature fields experienced by the other droplet. the results are expressed in terms of mobility coefficients $\underline{\underline{\mathbf{M}}}_{ij}$ defined as follows:

$$\mathbf{U}_1 = \underline{\underline{\mathbf{M}}}_{11} \cdot \mathbf{U}_1^{(o)} + \underline{\underline{\mathbf{M}}}_{12} \cdot \mathbf{U}_2^{(o)} \qquad [2a]$$

$$\underline{\underline{\mathbf{M}}}_{ij} = A_{ij}(r)\,\hat{\mathbf{e}}\hat{\mathbf{e}} + B_{ij}(r)\,[\underline{\underline{\mathbf{I}}} - \hat{\mathbf{e}}\hat{\mathbf{e}}], \qquad [2b]$$

where $\mathbf{U}_i^{(o)}$ is computed from [1]. In the analysis, the two droplets are assumed to have the same material properties ($\hat{k}$, $\hat{\eta}$) but may differ in size. Convective heat transfer is assumed negligible in solving for the temperature fields, and the Stokes equations are used to find the velocity fields. In the next section I consider the local fields which arise when a *single* droplet is placed in an undisturbed temperature field whose gradient is not necessarily constant over length scales comparable to the droplet radius. I prove that [1] also applies to a single droplet in a *nonuniform* temperature gradient. These results are then used in the subsequent section to alternately evaluate the effect of one droplet on the other. The coefficients A_{ij} and B_{ij} are determined in this manner with an error of $0(r^{-8})$, and the results are found in [26] and [29]. In the final section, my results are compared with the calculations of Meyyappan *et al.* (1983) for the special case of two bubbles which are aligned with the undisturbed temperature gradient. The two-droplet interactions derived here are then applied to theories of concentration effects on transport coefficients in dilute suspensions to obtain the $0(\phi)$ correction to the mean velocity, where ϕ is the volume fraction occupied by the droplets.

2. SINGLE DROPLET IN A TEMPERATURE FIELD

In order to apply the method of reflections to obtain the interactions between two droplets, as done in the next section, it is essential to understand the thermal and hydrodynamic effects of a single droplet in an arbitrary temperature field $T_A(\mathbf{x})$. The droplet is a sphere of radius a with internal thermal conductivity $\hat{k}$ and viscosity $\hat{\eta}$. The position of its center is $\mathbf{x}_o$, and the relative coordinate $\mathbf{r}$ equals $\mathbf{x} - \mathbf{x}_o$. Although $\mathbf{x}_o$ changes with time, the problem is considered quasi-steady, a good approximation if both the Peclet and Reynolds numbers are small. The undisturbed temperature field is assumed to satisfy Laplace's equation:

$$\nabla^2 T_A = 0. \qquad [3]$$

The validity of assuming a spherical shape for the droplet requires the viscous stresses on its surface be small relative to capillary forces: $\eta U/\gamma \ll 1$. Using [1] for U with $k^* = \eta^* = 0$ (a bubble), this constraint becomes

$$\frac{a}{\gamma}\left|\frac{\mathrm{d}\gamma}{\mathrm{d}T}\nabla T_A\right| \ll 1,$$

which will exist, even if ∇T_A varies over length scales of $0(a)$, as long as temperature differences across the poles of the droplet are sufficiently small to make $\Delta\gamma \ll \gamma$. In fact, the above constraint is generally less stringent than requiring the Reynolds number to be small.

In this section I first solve for the disturbance to T_A caused by the droplet, and then the droplet velocity and the velocity field in the surrounding fluid caused by thermally induced variations of interfacial tension at the surface.

Temperature field

The energy balance must be maintained inside and outside the droplet. Assuming convective transport is negligible, one has

$$(r < a) \qquad \nabla^2 \hat{T} = 0, \tag{4a}$$

$$(r > a) \qquad \nabla^2 T = 0, \tag{4b}$$

$$r = a: \qquad \hat{T} = T, \tag{5a}$$

$$\hat{k}\frac{\partial \hat{T}}{\partial r} = k\frac{\partial T}{\partial r} \tag{5b}$$

$$r \longrightarrow \infty: \qquad T \longrightarrow T_A. \tag{5c}$$

A solution to [4], which satisfies [5a] and [5c], is the following:

$$\hat{T} = T_A + \sum_{m=1}^{\infty}\left(\frac{r}{a}\right)^m S_m[\cdot]\lambda_m, \tag{6a}$$

$$T = T_A + \sum_{m=1}^{\infty}\left(\frac{a}{r}\right)^{m+1} S_m[\cdot]\lambda_m. \tag{6b}$$

The S_m are surface harmonics, defined by

$$\begin{aligned} S_m &= r^{m+1}(\nabla \ldots \nabla)^m (r^{-1}) \\ S_0 &= 1 \\ \mathrm{S}_1 &= -\frac{\mathbf{r}}{r} \\ \underline{\underline{S}}_2 &= 3\frac{\mathbf{r}\mathbf{r}}{r^2} - \underline{\underline{I}} \\ &\text{(etc.)} \end{aligned} \tag{7}$$

where $\underline{\underline{I}}$ is the unit dyadic. The λ_m are polyadic constants, and the symbol $[\cdot]$ denotes m scalar products using the inner nesting convention.

To determine λ_m, it is convenient to use the orthogonal property of surface harmonics:

$$\langle S_m S_j \rangle = 0 \qquad \text{if } m \neq j$$

The brackets denote an average over the area of a sphere of unit radius, expressed as follows in terms of integration over the spherical angles (θ, ϕ):

$$\langle f \rangle = \frac{1}{4\pi}\int\int f \sin\theta \, \mathrm{d}\theta \, \mathrm{d}\phi.$$

Substitution of [6] into [5b] shows

$$\lambda_1 = -\frac{(1-k^*)}{(2+k^*)}a(\nabla T_A)_o \qquad [8a]$$

$$\underline{\underline{\lambda}}_2 = \frac{(1-k^*)}{3(3+2k^*)}a^2(\nabla\nabla T_A)_o \qquad [8b]$$

where the subscript o denotes evaluation at $\mathbf{x} = \mathbf{x}_o$, and $k^* = \hat{k}/k$. The disturbance to the temperature field, $T' \equiv T - T_A$, is found by combining the foregoing expressions.

$$(r<a) \qquad \hat{T}' = \left(\frac{1-k^*}{2+k^*}\right)\mathbf{r}\cdot(\nabla T_A)_o + \left(\frac{1-k^*}{3+2k^*}\right)\mathbf{r}\,\mathbf{r}:(\nabla\nabla T_A)_o + 0(\nabla\nabla\nabla T_A)_o \qquad [9a]$$

$$(r>a) \qquad T' = \left(\frac{1-k^*}{2+k^*}\right)\left(\frac{a}{r}\right)^3\mathbf{r}\cdot(\nabla T_A)_o + \left(\frac{1-k^*}{3+2k^*}\right)\left(\frac{a}{r}\right)^5\mathbf{r}\,\mathbf{r}:(\nabla\nabla T_A)_o + 0(\nabla\nabla\nabla T_A)_o. \qquad [9b]$$

The gradient of T in the plane of the droplet surface, $\nabla_s T$, is needed to evaluate the stress in the next section; it is obtained by differentiating either of the above two expressions at $r = a$, adding the result to the Taylor expansion of ∇T_A about $\mathbf{x} = \mathbf{x}_o$, and eliminating the normal component.

$$\begin{aligned} r = a: \qquad \nabla_s T &= (\underline{\underline{I}} - \mathbf{n}\,\mathbf{n})\cdot\nabla T \\ &= \left(\frac{3}{2+k^*}\right)(\underline{\underline{I}} - \mathbf{n}\,\mathbf{n})\cdot(\nabla T_A)_o \\ &\quad + \left(\frac{5a}{3+2k^*}\right)(\underline{\underline{I}} - \mathbf{n}\,\mathbf{n})\mathbf{n}:(\nabla\nabla T_A)_o + 0(\nabla\nabla\nabla T_A)_o. \end{aligned} \qquad [10]$$

n is the unit normal vector at the droplet surface and points into the surrounding fluid.

Droplet velocity and velocity field in surrounding fluid

The interfacial tension is temperature dependent, so the tangential stress discontinuity at the droplet surface is

$$r = a: \qquad \nabla_s\gamma = \frac{\partial\gamma}{\partial T}\nabla_s T, \qquad [11]$$

with $\nabla_s T$ determined from [10]. Note that $\partial\gamma/\partial T$ is assumed constant on the scale of droplet radius. This stress creates motion which must satisfy the Stokes equations.

$$(r<a) \qquad \hat{\eta}\,\nabla^2\hat{\mathbf{v}} - \nabla\hat{p} = \mathbf{0}, \qquad [12a]$$

$$(r>a) \qquad \eta\,\nabla^2\mathbf{v} - \nabla p = \mathbf{0}, \quad \nabla\cdot\mathbf{v} = 0. \qquad [12b]$$

$$r = a: \qquad \hat{\mathbf{v}} = \mathbf{v}, \qquad [13a]$$

$$v_r = \mathbf{n}\cdot\mathbf{U}, \qquad [13b]$$

$$(\underline{\underline{I}} - \mathbf{n}\,\mathbf{n})\mathbf{n}:(\underline{\underline{\sigma}} - \hat{\underline{\underline{\sigma}}}) = -\nabla_s\gamma, \qquad [13c]$$

$$r \longrightarrow \infty: \qquad \mathbf{v} \longrightarrow \mathbf{0}. \qquad [13d]$$

U is the droplet velocity which is presently unknown. Boundary condition [13a] is not exact because interfacial forces accounting for γ are distributed over a small but nevertheless finite distance normal to the interface, as discussed by Anderson *et al.* (1982); however, [13a] is a very good approximation if $\hat{\eta}/\eta$ is not too large (say, $\hat{\eta}/\eta < 10^3$). Condition [13c] is a force balance in the plane of the interface, with $\underline{\underline{\sigma}}$ denoting the Newtonian stress dyadic. No force balance in the **n** direction is necessary because the droplet is assumed spherical.

A solution for $\hat{\mathbf{v}}$ and $\mathbf{v}$ can be constructed from Lamb's general solution as modified by Brenner (1964). The fields are described by the polyadic coefficients (α_m, β_m) which are determined from the following expressions:†

$$\mathbf{n} \cdot \mathbf{v}^{(a)} = \sum_{m=1}^{\infty} S_m[\cdot]\alpha_m, \tag{14a}$$

$$-r\nabla \cdot \mathbf{v}^{(a)} = \sum_{m=1}^{\infty} S_m[\cdot]\beta_m, \tag{14b}$$

where $\mathbf{v}^{(a)} = \mathbf{v}(r = a)$, the velocity on the droplet surface. By requiring α_m and β_m to be the same for internal and surrounding fluids, condition [13a] is automatically satisfied. From [13b] one has

$$\begin{aligned} \alpha_1 &= -\mathbf{U} \\ \underline{\alpha_m} &= \underline{0} \qquad \text{if } m > 1. \end{aligned} \tag{15}$$

The coefficients β_m must be determined by satisfying [13c]. Using the expressions for $\hat{\mathbf{v}}$ and $\mathbf{v}$ in terms of (α_m, β_m), as developed by Brenner (1964), [13c] becomes

$$\begin{aligned} &-\eta\left\{\sum_{m=1}^{\infty}\left[\frac{(m^2+2m+2)}{m(m+1)}r\nabla S_m[\cdot]\alpha_m + \frac{(2m+1)}{m(m+1)}r\nabla S_m[\cdot]\beta_m\right] - r\nabla \mathbf{S}_1 \cdot \alpha_1\right\} \\ &\quad + \hat{\eta}\left\{\sum_{m=1}^{\infty}\left[\frac{(m^2+1)}{m(m+1)}r\nabla S_m[\cdot]\alpha_m - \frac{(2m+1)}{m(m+1)}r\nabla S_m[\cdot]\beta_m\right] - r\nabla \mathbf{S}_1 \cdot \alpha_1\right\} \\ &\quad = \left(-\frac{\partial\gamma}{\partial T}\right)\nabla_s T, \end{aligned} \tag{16}$$

with $\nabla_s T$ obtained from [10]. By equating terms of equal orders in ∇S_m, one has

$$\beta_1 = \frac{1}{1+\eta^*}\left[\mathbf{U} + \frac{2}{2+k^*}\frac{a}{\eta}\left(-\frac{\partial\gamma}{\partial T}\right)(\nabla T_A)_o\right] \tag{17a}$$

$$\underline{\underline{\beta}}_2 = -\frac{1}{(1+\eta^*)(3+2k^*)}\left(-\frac{\partial\gamma}{\partial T}\right)\frac{a^2}{\eta}(\nabla\nabla T_A)_o, \tag{17b}$$

where $\eta^* = \hat{\eta}/\eta$.

In order to determine the droplet velocity, we must realize that the fluid force on any boundary enclosing the droplet is zero, since the temperature field produces no bulk (body) forces in the fluids. Suppose we take this imaginary boundary to be spherical with $r = R > a$. Then taking the limit $R \rightarrow a$ gives

$$\mathbf{F}_f = a^2 \iint_{R \rightarrow a} \mathbf{n} \cdot \underline{\underline{\sigma}} \sin\theta \, d\theta \, d\phi = \mathbf{0}. \tag{18}$$

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†It can be shown there are no rotational effects, that is, $\mathbf{r} \cdot (\nabla x \mathbf{v}^{(a)}) = 0$, since the temperature field exerts no couple on the droplet.

Brenner (1964) showed that

$$\mathbf{F}_f = 2\pi\eta a\,(3\alpha_1 + \beta_1). \qquad [19]$$

After combining [15], [17a], [18] and [19], one has

$$\mathbf{U} = \frac{2}{(2+k^*)(2+3\eta^*)}\,\frac{a}{\eta}\left(-\frac{\partial\gamma}{\partial T}\right)(\nabla T_A)_o, \qquad [20]$$

which is identical to [1] but applies to *any* T_A which satisfies [3]. The generality of [1] to nonuniform gradients has also been demonstrated by Subramanian (1985).

The velocity fields inside and outside the droplet are obtained by using expressions found in Brenner's paper. The only characteristic of the field inside which is needed in this paper is the volume-averaged value of $\hat{\mathbf{v}}$, which equals $\mathbf{U}$. The external field is given by the following which is correct to $O(\nabla\nabla T_A)$:

$$\begin{aligned}(r > a)\ \mathbf{v} = {} & \frac{1}{2}\left(\frac{a}{r}\right)^3\left(3\frac{\mathbf{rr}}{r^2} - \underline{\underline{\mathbf{I}}}\right)\cdot\mathbf{U} \\ & - \frac{3}{2}\,\frac{1}{(1+\eta^*)(3+2k^*)}\,\frac{a}{\eta}\left(-\frac{\partial\gamma}{\partial T}\right)\left(\frac{a}{r}\right)^3\frac{\mathbf{rrr}}{r^2} : (\nabla\nabla T_A)_o \\ & + \frac{1}{2}\,\frac{1}{(1+\eta^*)(3+2k^*)}\,\frac{a}{\eta}\left(-\frac{\partial\gamma}{\partial T}\right)\left(\frac{a}{r}\right)^5\left(5\frac{\mathbf{rrr}}{r^2} - 2\underline{\underline{\mathbf{I}}}\,\mathbf{r}\right) : (\nabla\nabla T_A)_o.\end{aligned} \qquad [21]$$

Note that while the primary field (first term on the right side) decays as r^{-3}, the secondary field, which is proportional to $\nabla\nabla T_A$, decays as r^{-2} and hence is longer range. The secondary field contributes to the interactions between droplets, as shown in the next section.

3. DERIVATION OF INTERACTIONS BETWEEN DROPLETS

An arbitrary configuration of two droplets is considered, with $\mathbf{r}_{12}$ being the vector from the center of droplet 1 to the center of droplet 2. The objective is to derive $\underline{\underline{\mathbf{M}}}_{ij}$, or A_{ij} and B_{ij} (see [2]), as a function of center-to-center distance r_{12}, physical properties such as k^* and η^* which are assumed the same for both droplets, and droplet radii a_1 and a_2 which could differ. The unit vector defining orientation of the two droplets is $\hat{\mathbf{e}} = \mathbf{r}_{12}/r_{12}$. The undisturbed temperature gradient (∇T_∞) is assumed to be constant over length scales comparable to r_{12}. The key results of the previous section, which are used below, are [9b], [20] and [21].

The coefficient $\underline{\underline{\mathbf{M}}}_{11}$ is considered first by setting $\partial\gamma/\partial T$ equal to zero for droplet 2 (i.e. $\mathbf{U}_2^{(o)} = \mathbf{0}$). There are three effects of droplet 2 which produce a change $\delta\mathbf{U}_1$ in the velocity of droplet 1:

$$\delta\mathbf{U}_1 = \delta\mathbf{U}_{21}^{(T)} + \delta\mathbf{U}_{121}^{(T)} + \delta\mathbf{U}_{121}^{(H)}.$$

$\delta\mathbf{U}_{21}^{(T)}$ is the change in $\mathbf{U}_1$ due to the disturbance (T_2') of the tempertaure field T_∞ caused by the presence of droplet 2. Using [9b] for T_2' and [20] for $\delta\mathbf{U}_{21}^{(T)}$, one has

$$\delta\mathbf{U}_{21}^{(T)} = -\left(\frac{1-k^*}{2+k^*}\right)\left(\frac{a_2}{r_{12}}\right)^3[3\,\hat{\mathbf{e}}\,\hat{\mathbf{e}} - \underline{\underline{\mathbf{I}}}]\cdot\mathbf{U}_1^{(o)}. \qquad [22]$$

$\delta\mathbf{U}_{121}^{(T)}$ is the result of reflecting the disturbance (T_1'), caused by droplet 1 interacting with T_∞, from droplet 2 back to droplet 1.

$$\delta\mathbf{U}_{121}^{(T)} = \left(\frac{1-k^*}{2+k^*}\right)^2\frac{(a_1a_2)^3}{r_{12}^6}[3\,\hat{\mathbf{e}}\,\hat{\mathbf{e}} + \underline{\underline{\mathbf{I}}}]\cdot\mathbf{U}_1^{(o)} + 0(r_{12}^{-8}). \qquad [23]$$

Finally, $\delta \mathbf{U}_{121}^{(H)}$ is the change in $\mathbf{U}_1$ produced by reflecting the velocity field caused by $\mathbf{U}_1^{(o)}$, called $\mathbf{v}_1$ here, from droplet 2 back to 1. Since the droplet is force free, the reflection is computed from the following (Batchelor 1970):

$$\delta \mathbf{U}_{121}^{(H)} = \frac{2 + 5\eta^*}{4(1 + \eta^*)} \frac{a_2^3}{r_{12}^2} \hat{\mathbf{e}}\,\hat{\mathbf{e}}\,\hat{\mathbf{e}} : [\nabla \mathbf{v}_1 + (\nabla \mathbf{v}_1)^T]_{\mathbf{r}=\mathbf{r}_{12}} + 0(r_{12}^{-4}\, \nabla \mathbf{v}_1, r_{12}^{-3}\, \nabla\nabla \mathbf{v}_1). \qquad [24]$$

Using [21] to evaluate $\mathbf{v}_1$ with $T_A = T_\infty$, one has

$$\delta \mathbf{U}_{121}^{(H)} = -\frac{3}{2}\left(\frac{2 + 5\eta^*}{1 + \eta^*}\right) \frac{(a_1 a_2)^3}{r_{12}^6} \hat{\mathbf{e}}\,\hat{\mathbf{e}} \cdot \mathbf{U}_1^{(o)} + 0(r_{12}^{-8}). \qquad [25]$$

After summing [22], [23] and [25] with the primary velocity $\underline{\underline{I}} \cdot \mathbf{U}_1^{(o)}$, the final results for A_{11} and B_{11}, as defined in [2], are obtained.

$$A_{11} = 1 - 2\left(\frac{1 - k^*}{2 + k^*}\right)\left(\frac{a_2}{r_{12}}\right)^3 + \left[4\left(\frac{1 - k^*}{2 + k^*}\right)^2 - \frac{3}{2}\left(\frac{2 + 5\eta^*}{1 + \eta^*}\right)\right] \frac{(a_1 a_2)^3}{r_{12}^6} + 0(r_{12}^{-8}) \qquad [26a]$$

$$B_{11} = 1 + \left(\frac{1 - k^*}{2 + k^*}\right)\left(\frac{a_2}{r_{12}}\right)^3 + \left(\frac{1 - k^*}{2 + k^*}\right)^2 \frac{(a_1 a_2)^3}{r_{12}^6} + 0(r_{12}^{-8}). \qquad [26b]$$

The mobility $\underline{\underline{\mathbf{M}}}_{12}$ is now evaluated by setting $\partial\gamma/\partial T = 0$ for droplet 1 (i.e. $\mathbf{U}_1^{(o)} = \mathbf{0}$), and examining the velocity field produced by droplet 2 as it moves in response to ∇T_∞. The primary velocity field caused by movement of droplet 2 at $\mathbf{U}_2^{(o)}$, denoted by $\mathbf{v}_2$ and calculated from [21] with $T_A = T_\infty$, convects droplet 1 at a rate given by Faxen's law as modified by Hetsroni *et al.* (1971) for fluid particles:

$$\delta \mathbf{U}_{21}^{(H)} = \mathbf{v}_2 \Big|_{\mathbf{r}=-\mathbf{r}_{12}} + a_1^2 \frac{\eta^*}{4 + 6\eta^*} (\nabla^2 \mathbf{v}_2) \Big|_{\mathbf{r}=-\mathbf{r}_{12}} = \frac{1}{2}\left(\frac{a_2}{r_{12}}\right)^3 [3\hat{\mathbf{e}}\hat{\mathbf{e}} - \underline{\underline{I}}] \cdot \mathbf{U}_2^{(o)}. \qquad [27]$$

A second effect arises because the disturbance (T_1') of the temperature field T_∞ by droplet 1 interacts with droplet 2 to create a velocity field, determined from [21] with $T_A = T_1'$, which convects droplet 1. The change in the velocity of droplet 1 caused by this effect is

$$\begin{aligned} \delta \mathbf{U}_{121}^{(T,H)} = \Bigg\{ &-\frac{1}{2}\left(\frac{1 - k^*}{2 + k^*}\right) [\underline{\underline{I}} + 3\hat{\mathbf{e}}\hat{\mathbf{e}}] \\ &+ \frac{9}{2}\left(\frac{1 - k^*}{3 + 2k^*}\right)\left(\frac{2 + 3\eta^*}{1 + \eta^*}\right)\hat{\mathbf{e}}\hat{\mathbf{e}}\Bigg\} \frac{(a_1 a_2)^3}{r_{12}^6} \cdot \mathbf{U}_2^{(o)} + 0(r_{12}^{-8}). \end{aligned} \qquad [28]$$

$\underline{\underline{\mathbf{M}}}_{12}$ is obtained by summing [27] and [28] and factoring $\mathbf{U}_2^{(o)}$. The scalar coefficients in [2] are

$$A_{12} = \left(\frac{a_2}{r_{12}}\right)^3 - \left[2\left(\frac{1 - k^*}{2 + k^*}\right) - \frac{9}{2}\left(\frac{1 - k^*}{3 + 2k^*}\right)\left(\frac{2 + 3\eta^*}{1 + \eta^*}\right)\right] \frac{(a_1 a_2)^3}{r_{12}^6} + 0(r_{12}^{-8}) \qquad [29a]$$

$$B_{12} = -\frac{1}{2}\left(\frac{a_2}{r_{12}}\right)^3 - \frac{1}{2}\left(\frac{1 - k^*}{2 + k^*}\right) \frac{(a_1 a_2)^3}{r_{12}^6} + 0(r_{12}^{-8}). \qquad [29b]$$

These expressions, along with [26], form the main results of this paper.

Two limiting cases are now considered. First, let both droplets be *equal in size;* hence they move at the same velocity (U) at any configuration.

$$\mathbf{U} = A(r_{12})\hat{\mathbf{e}}\hat{\mathbf{e}} + B(r_{12})[\underline{\underline{I}} - \hat{\mathbf{e}}\hat{\mathbf{e}}] \qquad [30a]$$

$$A = A_{11} + A_{12} = 1 + \frac{3k^*}{2 + k^*}\left(\frac{a}{r_{12}}\right)^3 - \left[\frac{6k^*(1 - k^*)}{(2 + k^*)^2} + \frac{3}{2}\frac{(10k^* + 6\eta^* + 19k^*\eta^*)}{(1 + \eta^*)(3 + 2k^*)}\right]\left(\frac{a}{r_{12}}\right)^6 + 0(r_{12}^{-8}), \qquad [30b]$$

$$B = B_{11} + B_{12} = 1 - \frac{3k^*}{2(2 + k^*)}\left(\frac{a}{r_{12}}\right)^3 - \frac{3}{2}\frac{k^*(1 - k^*)}{(2 + k^*)^2}\left(\frac{a}{r_{12}}\right)^6 + 0(r_{12}^{-8}). \qquad [30c]$$

In the second case, let both droplets be "bubbles" ($k^* \longrightarrow 0$, $\eta^* \longrightarrow 0$) which could be of different size. Then,

$$A_{11} = 1 - \left(\frac{a_2}{r_{12}}\right)^3 - 2\frac{(a_1a_2)^3}{r_{12}^6} + 0(r_{12}^{-8}), \qquad [31a]$$

$$A_{12} = \left(\frac{a_2}{r_{12}}\right)^3 + 2\frac{(a_1a_2)^3}{r_{12}^6} + 0(r_{12}^{-8}), \qquad [31b]$$

$$B_{11} = 1 + \frac{1}{2}\left(\frac{a_2}{r_{12}}\right)^3 + \frac{1}{4}\frac{(a_1a_2)^3}{r_{12}^6} + 0(r_{12}^{-8}), \qquad [31c]$$

$$B_{12} = -\frac{1}{2}\left(\frac{a_2}{r_{12}}\right)^3 - \frac{1}{4}\frac{(a_1a_2)^3}{r_{12}^6} + 0(r_{12}^{-8}). \qquad [31d]$$

These results agree with the $0(r_{12}^{-3})$ derivations by Meyyappan & Subramanian (1984). If the bubbles are of *equal size* (so $\mathbf{U}_1^{(o)} = \mathbf{U}_2^{(o)}$),

$$A = A_{11} + A_{12} = 1$$

$$B = B_{11} + B_{12} = 1$$

and hence

$$\mathbf{U} = \mathbf{U}^{(o)}, \qquad [32]$$

at least to $0(r_{12}^{-6})$. Meyyappan *et al.* (1983) show this result to be exact at all separations when the bubbles are aligned with the temperature gradient.

4. DISCUSSION

The interaction between two droplets results from two phenomena: each droplet disturbs the local temperature field experienced by the other, and the movement of each drags surrounding fluid which convects the other droplet. The interaction is relatively weak, of $0(r_{12}^{-3})$ in the leading term, because both the temperature and velocity disturbances of each drop decay like r^{-3}. For comparison, the leading order of interaction between two Stokeslets is $0(r_{12}^{-1})$; hence, the interaction between droplets undergoing sedimentation is much stronger than droplets moving by the Marangoni effect.

My results for bubbles, [31], can be compared with the calculations of Meyyappan *et al.* (1983) by considering movement when $\hat{\mathbf{e}}$ is parallel to ∇T_∞. The velocity of bubble 1 in this parallel alignment is

$$\frac{U_1^{(11)}}{U_1^{(o)}} = A_{11} + \frac{a_2}{a_1}A_{12} = 1 + \left(\frac{a_2}{a_1} - 1\right)\left(\frac{a_2}{r_{12}}\right)^3 + 2\left(\frac{a_1}{a_2}\right)^2\left(1 - \frac{a_1}{a_2}\right)\left(\frac{a_2}{r_{12}}\right)^6 + 0(r_{12}^{-8}). \qquad [33]$$

Table 1 compares this equation, with the $0(r_{12}^{-8})$ term neglected, with the calculations of Meyyappan *et al.* for $a_1/a_2 = 0.5$. The agreement is quite good even for a_2/r_{12} as large as 0.606 ($a_2/r_{12} = 0.667$ when the bubbles touch), indicating the higher order terms such as $0(r_{12}^{-8})$ are not important unless the bubbles are very near contact. In fact, by using only the $0(r_{12}^{-3})$ term of [33] which was derived by Meyyappan & Subramanian (1984), there obtains a reasonably good approximation when $a_2/r_{12} < 0.5$. This favorable comparison is encouraging in the sense it implies the general results for arbitrary k^*, η^* and a_1/a_2 are quite accurate for a large range of separations.

The details of two-droplet interactions can be used to find how the mean velocity of a suspension of droplets is affected by the volume fraction (ϕ) of the droplets.

$$\langle \mathbf{U} \rangle = [1 + \kappa\phi + 0(\phi^2)]\mathbf{U}^{(o)}. \qquad [34]$$

Assume all droplets are the same size. The theory of incorporating two-body hydrodynamic information to obtain κ is described elsewhere (Batchelor 1972, Anderson & Reed 1980, Glendinning & Russel 1982). Because the suspension is bounded, the volume-averaged velocity and temperature fields must obey the following:

$$\int_V \mathbf{v}\,\mathrm{d}V = \mathbf{0}, \quad \int_V \nabla T\,\mathrm{d}V = \nabla T_\infty, \qquad [35]$$

where V denotes the entire volume of the suspension. These mean fields are added and subtracted in judiciously chosen places to allow the results for *unbounded* systems, which were derived in the previous two sections, to be applied to a *bounded* suspension. The expression for κ is

$$\kappa\mathbf{U}^{(o)} = \frac{3}{4\pi a^3}\left\{\int_V \mathbf{v}_1(\mathbf{r})[g(\mathbf{r}) - 1]\,\mathrm{d}\mathbf{r} + \frac{2}{(2 + k^*)(2 + 3\eta^*)}\frac{a}{\eta}\left(\frac{-\partial\gamma}{\partial T}\right)\int_V \nabla T_1'(\mathbf{r})[g(\mathbf{r}) - 1]\,\mathrm{d}\mathbf{r} + \int_V \mathbf{W}(\mathbf{r})g(\mathbf{r})\,\mathrm{d}\mathbf{r}\right\}. \qquad [36]$$

$\mathbf{v}_1$ is the fluid velocity and T_1' the temperature disturbance ($T - T_\infty$) caused by a single droplet at $\mathbf{r} = \mathbf{0}$ in the constant undisturbed gradient ∇T_∞; $\mathbf{v}_1$ and T_1' are computed from [21] and [9b], respectively, with $T_A = T_\infty$. $\mathbf{W}$ is a "correction factor" given by

$$\mathbf{W} = \mathbf{U}(\mathbf{r}) - \left[\mathbf{U}^{(o)} + \mathbf{v}_1 + \frac{2}{(2 + k^*)(2 + 3\eta^*)}\frac{a}{\eta}\left(\frac{-\partial\gamma}{\partial T}\right)\nabla T_1'\right] \qquad [37]$$

where $\mathbf{U}(\mathbf{r})$ is the velocity of the droplet of $\mathbf{r}$ given a neighbor at $\mathbf{0}$. Note that $\mathbf{W}$ is $0(r^{-6})$ and hence converges when integrated over the entire volume ($r \longrightarrow \infty$).

One of the significant problems in determining suspension properties, such as κ, is that

Table 1. Two bubbles aligned with the temperature gradient; $a_1/a_2 - 0.5$

	$U_1U_1^{(0)}$		$U_2/U_2^{(0)}$	
a_2/r_{12}	Eq. [33]	Lit.†	Eq. [33]‡	Lit.†
0.60606	1.23500	1.26894	0.97989	0.97675
0.55556	1.17882	1.19107	0.98561	0.98447
0.50000	1.12891	1.13304	0.99023	0.98986
0.44444	1.08972	1.09105	0.99355	0.99343
0.40000	1.06502	1.06553	0.99549	0.99544
0.22222	1.01100	1.01101	0.99930	0.99930
0.15385	1.00364	1.00364	0.99977	0.99977

†Meyyappan *et al.* (1983)

‡To obtain $U_2/U_2^{(0)}$ from equation [33], replace a_1/a_2 by a_2/a_1, and a_2/r_{12} by a_1/r_{12}

the two-particle distribution function, $g(\mathbf{r})$, could depend on the applied forces such as ∇T_∞; Batchelor (1974) discusses this point. For identical particles which experience negligible long-range forces, a "hard sphere" distribution is appropriate:

$$\begin{aligned} g &= 0 \quad \text{if} \quad r < 2a \\ &= 1 \quad \text{if} \quad r > 2a. \end{aligned} \qquad [38]$$

To achieve uniformity at $r > 2a$, the particles must be sufficiently small that Brownian motion dominates any multiparticle hydrodynamic interactions which might tend to impart microscopic structure to the suspension. The zero value for $r < 2a$ is simply an excluded volume effect. By combining [36]–[38] and using the results of the previous sections, namely [2], [26] and [29] for $\mathbf{U}$, [21] for $\mathbf{v}_1$ and [9b] for T_1' with $T_A = T_\infty$, I obtain

$$\kappa = -\frac{3}{2+k^*} - \frac{1}{24}\left[\frac{9k^*(1-k^*)}{(2+k^*)^2} + \frac{3}{2}\,\frac{(10k^* + 6\eta^* + 19k^*\eta^*)}{(1+\eta^*)(3+2k^*)}\right]. \qquad [39]$$

This result is not exact, even given that [38] holds, because $0(r^{-8})$ terms are neglected in $\mathbf{W}$; however, the error should be small. κ is always *negative*, so the mean velocity of a suspension is lower than for a single droplet.

As examples of limiting situations, consider 1) bubbles ($k^* = \eta^* = 0$), 2) viscous, insulating droplets ($k^* = 0, \eta^* \rightarrow \infty$), and 3) viscous, conducting droplets ($k^* \rightarrow \infty, \eta^* \rightarrow \infty$). Using [39] one has

$$\kappa_1 = -\frac{3}{2}, \kappa_2 = -\frac{13}{8}, \kappa_3 = -\frac{7}{32} \qquad [40]$$

Note that for bubbles κ is non-zero, even though there is no interaction between two equal-sized bubbles in an *unbounded* fluid. The reason for this is that in the bounded suspension the volume-averaged flow is zero (this contributes -1 to κ) and the mean temperature gradient is ∇T_∞ (this contributes $-\frac{1}{2}$ to κ). The results in [40] show that, in any case, the magnitude of κ is small relative to what is found for sedimentation of droplets (Anderson & Reed 1980):

$$\begin{aligned} \kappa_{\text{sed}} &= -4.0 \qquad (\eta^* \rightarrow 0) \\ &= -6.5 \qquad (\eta^* \rightarrow \infty) \end{aligned} \qquad [41]$$

The larger magnitude for sedimentation is due to the $0(r_{12}^{-1})$ hydrodynamic interactions, that is, a sedimenting droplet carries more surrounding fluid with it than does a droplet moving by capillary effects.

The analysis presented here used a method of reflections which was truncated after the $O(r_{12}^{-6})$ effects, and the general result for unbounded systems is given by [2], [26] and [29]. One more reflection of thermal and hydrodynamic fields could be applied to obtain the $O(r_{12}^{-8})$ interactions, but the numerical significance would be small except in the limit when the droplets are nearly touching. In the limit of touching, the expansions in $O(r_{12}^{n})$ may not converge, so there is little incentive to extend the expansion.

NOMENCLATURE

a	droplet radius (m)
A_{ij}	interaction coefficient defined by [2b]
B_{ij}	interaction coefficient defined by [2b]

$\hat{e}$	$\mathbf{r}_{12}/r_{12}$
$g(\mathbf{r})$	normalized probability of finding a second droplet at $\mathbf{r}$ given the first droplet at $\mathbf{0}$
$\underline{\underline{\mathrm{I}}}$	unit dyadic
k	thermal conductivity (J m^{-1} s^{-1} K^{-1})
k^*	$\hat{k}/\mathrm{k}$
$\underline{\underline{\mathrm{M}}}_{ij}$	interaction dyadic defined by [2a]
$\mathbf{n}$	$\mathbf{r}/r$ at the droplet surface
p	pressure (N m^{-2})
$\mathbf{r}$	$\mathbf{x} - \mathbf{x}_0$ (m)
$\mathbf{r}_{12}$	vector from center of droplet 1 to center of droplet 2 (m)
S_m	surface harmonics defined by [7]
T	temperature (K)
$\mathbf{U}$	velocity of a droplet (m s^{-1})
$\mathbf{v}$	velocity field in the fluids (m s^{-1})
$\mathbf{W}$	correction to velocity interaction defined by [37] (m s^{-1})
$\mathbf{x}$	position vector (m)
$\mathbf{x}_0$	position of center of droplet (m)
α_m	polyadic constant of order m defined by [14a] (m s^{-1})
β_m	polyadic constant of order m defined by [14b] (m s^{-1})
γ	interfacial tension (N m^{-1})
η	coefficient of viscosity (kg m^{-1} s^{-1})
η^*	$\hat{\eta}/\eta$
κ	$O(\phi)$ coefficient defined in [34]
λ_m	polyadic constant defined by [6] (m s^{-1})
$\underline{\underline{\sigma}}$	Newtonian stress dyadic (N m^{-2})
ϕ	volume fraction of droplets

Note: ˆ over variable denotes property inside droplet. Subscript o on gradient operations denotes evaluation at $\mathbf{x} = \mathbf{x}_0$.

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