Journal of Engineering Mathematics **30:** 299–305, 1996.

Thermocapillary mobility of bubbles and electrophoretic motion of particles in a fluid *

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Received 15 September, 1995

Abstract. It is shown that for a collection of equal-sized bubbles in a viscous incompressible fluid, that is subjected to a spatially harmonic temperature field, a solution of the steady Stokes equations exists for which the flow velocity everywhere is irrotational and proportional to the local temperature gradient. Moreover, the bubbles remain at rest. As a consequence, for a suspension of equal-sized bubbles, which on average is spatially uniform, the effective thermocapillary mobility tensor is identical to the effective thermal conductivity tensor, apart from a simple proportionality factor. Analogous results hold for the electrophoretic motion of equal-sized particles in an electrolyte solution, provided the Debye length of the solution is much less than the particle radius.

1. Introduction

A bubble in a liquid with a temperature gradient will move in the direction of higher temperature due to the temperature dependence of the surface tension [1]. The motion of a collection of bubbles is complicated, because then both the temperature field and the flow field are intricate functions of position. It has been shown by Acrivos, Jeffrey, and Saville [2] that for a collection of equal-sized bubbles placed in a uniform temperature gradient a significant simplification occurs. In this case the local flow velocity differs from the gradient of the temperature perturbation only by a constant factor. Hence the flow is irrotational, and the pressure perturbation vanishes. Each bubble moves as if it were by itself in the fluid. This remarkable theorem was derived as a generalization of explicit results for the case of two bubbles [3, 4, 5, 6] Analogous results hold for the electrophoretic motion of equal-sized spheres in the limit of thin double layers. In this limit the two problems are mathematically identical [2].

In the following we generalize the theorem of Acrivos *et al.* [2]. We show that for a collection of equal-sized bubbles placed in a temperature field which is a solution of Laplace's equation a solution of the Stokes equations exists which satisfies the boundary conditions at the surface of the bubbles, for which the flow velocity differs from the local temperature gradient only by a constant factor, and for which all bubbles remain at rest. For a uniform imposed temperature gradient the solution is related to the situation studied by Acrivos et al. [2] by a Galilean transformation.

The theorem we derive is important, since it allows a simple discussion of the macroscopic transport properties of a suspension of equal-sized bubbles. On a macroscopic length scale the variation of the average temperature field may be calculated from an analogue with electrostatics, the temperature playing the role of electrostatic potential, and the effective thermal conductivity tensor replacing the dielectric tensor. It follows from Maxwell's theory that the average field depends significantly on the shape of the macroscopic sample. Nonetheless, the effective dielectric tensor is a well-defined transport property, independent of sample shape

* See note on page 304

and determined by the local microgeometry [7]. Our theorem shows that the effective thermocapillary mobility tensor differs from the effective thermal conductivity tensor only by a simple factor.

2. Single bubble

We consider first a single spherical bubble of radius a, centered at the origin, and immersed in a viscous incompressible fluid with shear viscosity η and thermal conductivity λ. The surface tension γ of the bubble is assumed so large that the bubble is kept spherical at all times. The temperature field $T(\boldsymbol{r})$ satisfies Laplace's equation $\nabla^2 T = 0$ both inside and outside the bubble. Since the thermal conductivity inside the bubble is negligibly small, the boundary condition $\partial T/\partial r = 0$ at $r = a+$ applies. The temperature is continuous at the bubble surface. These conditions define a unique temperature field, once the behavior at infinity is specified. We consider the imposed temperature field

$$T_0(\boldsymbol{r}) = r^\ell \hat{Y}_{\ell m}(\theta, \varphi), \tag{2.1}$$

in spherical coordinates (r, θ, φ), with the spherical harmonic [8, p 24]

$$\hat{Y}_{\ell m}(\theta, \varphi) = (-1)^m P_\ell^m(\cos\theta) e^{im\varphi}. \tag{2.2}$$

To facilitate comparison with earlier work [9], we omit the normalization factor, as indicated by the hat. The complete temperature field is

$$\begin{aligned} T(\boldsymbol{r}) &= \left[r^\ell + \frac{\ell}{\ell+1} \frac{a^{2\ell+1}}{r^{\ell+1}} \right] \hat{Y}_{\ell m}(\theta, \varphi), \qquad && r > a, \\ &= \frac{2\ell+1}{\ell+1} r^\ell \hat{Y}_{\ell m}(\theta, \varphi), && r < a. \end{aligned} \tag{2.3}$$

The variation of the temperature field on the bubble surface causes a motion of the outside fluid via the thermocapillary effect associated with the temperature dependence of the surface tension γ. The velocity field $\boldsymbol{v}(\boldsymbol{r})$ and the pressure field $p(\boldsymbol{r})$ of the outer fluid are assumed to satisfy the Stokes equations

$$\eta \nabla^2 \boldsymbol{v} - \nabla p = 0, \qquad \nabla \cdot \boldsymbol{v} = 0. \tag{2.4}$$

The first equation may be expressed as $\nabla \cdot \boldsymbol{\sigma} = 0$, where $\boldsymbol{\sigma}$ is the stress tensor with components

$$\sigma_{\alpha\beta} = \eta \left(\frac{\partial v_\alpha}{\partial x_\beta} + \frac{\partial v_\beta}{\partial x_\alpha} \right) - p\delta_{\alpha\beta}. \tag{2.5}$$

Since the bubble is kept spherical, the velocity field satisfies the kinematic condition

$$v_r\big|_{a+} = U_r, \tag{2.6}$$

where $\boldsymbol{U}$ is the translational velocity of the bubble. In linear approximation the surface tension varies along the surface as

$$\gamma(\theta, \varphi) = \gamma_0 + \frac{\partial \gamma}{\partial T} [T(a, \theta, \varphi) - T_{eq}], \tag{2.7}$$

where $\gamma_0(T_{eq})$ is the surface tension at the equilibrium temperature T_{eq}. The normal-tangential components of the stress tensor satisfy the boundary condition [10, p 302]

$$\sigma_{rt}\big|_{a+} = \frac{\partial\gamma}{\partial T}\nabla_t T\big|_a, \tag{2.8}$$

where ∇_t denotes the tangential derivative. The conditions expressed by Eqs. (2.6) and (2.8) suffice to determine the velocity and pressure fields. Imposing $\boldsymbol{U} = 0$ we find

$$\begin{aligned} \boldsymbol{v}_T(\boldsymbol{r}) &= -\xi a^{2\ell-1}\left[\frac{2\ell(2\ell-1)(2\ell+1)}{\ell+1}\boldsymbol{v}^-_{\ell m0}(\boldsymbol{r}) + (2\ell+1)^2(2\ell+3)a^2\boldsymbol{v}^-_{\ell m2}(\boldsymbol{r})\right], \\ p_T(\boldsymbol{r}) &= -\xi\eta\frac{2\ell(2\ell-1)}{\ell+1}\frac{a^{2\ell-1}}{r^{\ell+1}}\hat{Y}_{\ell m}(\theta,\varphi), \qquad r > a, \end{aligned} \tag{2.9}$$

with velocity fields $\boldsymbol{v}^-_{\ell m\sigma}(\boldsymbol{r})$ in standard notation [9], and with coefficient

$$\xi = -\frac{1}{2}\frac{a}{\eta}\frac{\partial\gamma}{\partial T}. \tag{2.10}$$

For $\ell = 1$ the velocity field $\boldsymbol{v}^-_{1m0}(\boldsymbol{r})$ decays with distance as $1/r$. This shows that for $\ell = 1$, in order to keep the bubble stationary, an external force must be applied. For uniform temperature gradient $\boldsymbol{g}_T$, corresponding to

$$T_0(\boldsymbol{r}) = \boldsymbol{g}_T\cdot\boldsymbol{r}, \tag{2.11}$$

this force is given by

$$\boldsymbol{E}_T = -4\pi\eta a\xi\boldsymbol{g}_T. \tag{2.12}$$

For free motion the bubble moves with velocity

$$\boldsymbol{U} = \xi\boldsymbol{g}_T, \tag{2.13}$$

and the velocity and pressure fields are

$$\boldsymbol{v}(\boldsymbol{r}) = \frac{1}{2}\frac{a^3}{r^3}(3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}} - \mathbf{1})\cdot\boldsymbol{U}, \qquad p(\boldsymbol{r}) = 0. \tag{2.14}$$

This shows that the effect of a uniform temperature gradient on a free bubble is to induce a stresslet, and a translational velocity, but no force.

Since for $\ell > 1$ the velocity $\boldsymbol{U}$ vanishes, Eq. (2.13) may be generalized to [5, 11]

$$\boldsymbol{U} = \mu^{tc}(1)(\nabla T_0)_O, \qquad \mu^{tc}(1) = \xi, \tag{2.15}$$

where $\mu^{tc}(1)$ is the single-bubble thermocapillary mobility. We have chosen signs such that ξ is positive for $\partial\gamma/\partial T$ negative.

3. Imposed flow

Next we consider the bubble in the absence of a temperature field, but in the presence of an imposed flow field. Let the imposed flow field be

$$\boldsymbol{v}_0(\boldsymbol{r}) = \boldsymbol{v}^+_{\ell m0}(\boldsymbol{r}), \qquad p_0(\boldsymbol{r}) = 0, \tag{3.1}$$

again in the notation used previously [9]. The imposed flow is a potential flow, since

$$\boldsymbol{v}^{+}_{\ell m0}(\boldsymbol{r}) = \nabla(r^{\ell}\hat{Y}_{\ell m}(\theta,\varphi)). \tag{3.2}$$

The modification, due to the presence of the bubble, is [9, 12]

$$\begin{aligned} \boldsymbol{v}_V(\boldsymbol{r}) &= -\frac{2\ell(2\ell-1)(2\ell+1)}{\ell+1}a^{2\ell-1}\boldsymbol{v}^{-}_{\ell m0}(\boldsymbol{r}), \\ p_V(\boldsymbol{r}) &= -\eta\frac{2\ell(2\ell-1)}{\ell+1}\frac{a^{2\ell-1}}{r^{\ell+1}}\hat{Y}_{\ell m}(\theta,\varphi), \qquad r > a. \end{aligned} \tag{3.3}$$

For $\ell = 1$ the bubble does not move, which requires an applied force.

By comparison with Eq. (2.9) we see that superposition of the two imposed fields

$$T_0(\boldsymbol{r}) = r^{\ell}\hat{Y}_{\ell m}(\hat{\boldsymbol{r}}), \qquad \boldsymbol{v}_0(\boldsymbol{r}) = -\xi\nabla T_0(\boldsymbol{r}), \tag{3.4}$$

leads to the flow perturbation

$$\begin{aligned} \boldsymbol{v}_T(\boldsymbol{r}) - \xi\boldsymbol{v}_V(\boldsymbol{r}) &= -\xi a^{2\ell+1}(2\ell+1)^2(2\ell+3)\boldsymbol{v}^{-}_{\ell m2}(\boldsymbol{r}), \\ p_T(\boldsymbol{r}) - \xi p_V(\boldsymbol{r}) &= 0, \qquad r > a. \end{aligned} \tag{3.5}$$

This is a surprisingly simple result. The pressure perturbation vanishes, and the velocity perturbation can be derived from a potential, since [9]

$$\boldsymbol{v}^{-}_{\ell m2}(\boldsymbol{r}) = \frac{\ell}{(\ell+1)(2\ell+1)^2(2\ell+3)}\nabla\left(\frac{1}{r^{\ell+1}}\hat{Y}_{\ell m}(\theta,\varphi)\right). \tag{3.6}$$

A comparison with Eq. (2.3) shows that the flow perturbation is related to the temperature perturbation for $r > a$ by

$$\boldsymbol{v}'(\boldsymbol{r}) = -\xi\nabla T'(\boldsymbol{r}), \qquad r > a. \tag{3.7}$$

Hence these fields are related in the same way as the incident fields in Eq. (3.4).

More generally, if an arbitrary imposed harmonic temperature field $T_0(\boldsymbol{r})$ is combined with the imposed flow

$$\boldsymbol{v}_0(\boldsymbol{r}) = -\xi\nabla T_0(\boldsymbol{r}), \qquad p_0(\boldsymbol{r}) = 0, \tag{3.8}$$

then the complete temperature and flow fields can be expressed as

$$T(\boldsymbol{r}) = T_0(\boldsymbol{r}) + T'(r), \qquad \boldsymbol{v}(\boldsymbol{r}) = \boldsymbol{v}_0(\boldsymbol{r}) + \boldsymbol{v}'(\boldsymbol{r}) \tag{3.9}$$

with perturbed fields $T'(\boldsymbol{r})$ and $\boldsymbol{v}'(\boldsymbol{r})$ that are related as in Eq. (3.7), and with vanishing pressure field.

We consider the case $\ell = 1$ separately. The imposed flow $\boldsymbol{v}^{+}_{1m0}(\boldsymbol{r})$ is spatially uniform. In the derivation of Eq. (3.3) it was assumed that the bubble center is kept fixed at the origin. It is evident from Eq. (3.5) that the combination

$$T_0(\boldsymbol{r}) = \boldsymbol{g}_T\cdot\boldsymbol{r}, \qquad \boldsymbol{v}_0 = -\xi\boldsymbol{g}_T \tag{3.10}$$

leads to a bubble at rest without exertion of force. The resulting flow perturbation

$$\boldsymbol{v}'(\boldsymbol{r}) = \frac{1}{2}\xi\frac{a^3}{r^3}(3\hat{\boldsymbol{r}}\hat{\boldsymbol{r}} - \mathbf{1})\cdot\boldsymbol{g}_T \tag{3.11}$$

is dipolar, and is identical to that in Eq. (2.14), as one would expect from Galilean invariance.

4. Many bubbles

The results derived in the preceding section can be extended straightforwardly to the case of many bubbles. Thus we consider N spherical bubbles of radius a suspended in arbitrary configuration in an infinite viscous incompressible fluid. It is essential to consider identical bubbles, since the coefficient ξ, as given by Eq. (2.10), is proportional to the bubble radius. We consider again an imposed harmonic temperature field $T_0(\boldsymbol{r})$, and combine this with the incident flow $\boldsymbol{v}_0(\boldsymbol{r}) = -\xi\nabla T_0(\boldsymbol{r})$, $p_0(\boldsymbol{r}) = 0$, as in Eq. (3.8). We denote the joint bubble volume as V_0, and the complementary space as $\overline{V}$. The complete temperature and flow fields can be expressed as in Eq. (3.9). The temperature perturbation $T'(\boldsymbol{r})$ and the flow perturbation $\boldsymbol{v}'(\boldsymbol{r})$ in the complementary space $\overline{V}$ are related as in Eq. (3.7),

$$\boldsymbol{v}'(\boldsymbol{r}) = -\xi\nabla T'(\boldsymbol{r}), \qquad \boldsymbol{r} \in \overline{V}. \tag{4.1}$$

This follows immediately from a multiple scattering analysis by use of the single bubble results of Sec. 3. The pressure perturbation vanishes, and every bubble is at rest and experiences no force.

The solution found above is a generalization of that of Acrivos *et al.* [2]. These authors considered a situation, where the temperature gradient at infinity is uniform, and the flow field vanishes at infinity. In that case the bubbles move with the single bubble velocity given by Eq. (2.13). After a Galilei transformation to a system where the bubbles are at rest, the solution is a special case in the class considered above.

The present formulation allows a transparent discussion of the relation between two macroscopic transport coefficients characterizing the average flow of heat and the average motion of bubbles in a suspension. Thus we consider a large number N of identical bubbles, distributed approximately uniformly in a volume Ω of simple shape, and immersed in infinite fluid. At first we omit the thermocapillary effect, and study the pure thermal conductivity problem. The effective thermal conductivity λ_{eff}, or, more generally, the effective thermal conductivity tensor $\boldsymbol{\lambda}_{\text{eff}}$ in case the suspension is microscopically anisotropic, is defined as the tensor of coefficients in the macroscopic relation

$$<\boldsymbol{j}> = -\boldsymbol{\lambda}_{\text{eff}} \cdot <\nabla T>, \tag{4.2}$$

where $\boldsymbol{j}$ is the thermal current density

$$\begin{aligned} \boldsymbol{j}(\boldsymbol{r}) &= -\lambda\nabla T \quad \text{for} \quad \boldsymbol{r} \in \overline{V}, \\ &= \quad 0 \qquad \text{for} \quad \boldsymbol{r} \in V_0, \end{aligned} \tag{4.3}$$

and the averages in Eq. (4.2) are over the probability distribution of bubble configurations. In the thermodynamic limit $N \to \infty$, $\Omega \to \infty$ at constant density $n = N/\Omega$ the tensor $\boldsymbol{\lambda}_{\text{eff}}$ takes a well-defined value independent of the shape of Ω, and may be expressed as a sum of absolutely convergent integrals over the set of microscopic distribution functions [7, 13]. Accurate values have been determined for a hard sphere distribution by computer simulation [14].

Similarly, the effective thermocapillary mobility tensor $\boldsymbol{\mu}^{tc}_{\text{eff}}$ is defined by

$$<\boldsymbol{U}> - <\boldsymbol{v}> = \boldsymbol{\mu}^{tc}_{\text{eff}} \cdot <\nabla T>. \tag{4.4}$$

For the situations considered above the mean bubble velocity vanishes, $< \boldsymbol{U} >= 0$, and the mean flow velocity is given by

$$< \boldsymbol{v} >= \frac{\xi}{\lambda} < \boldsymbol{j} > . \tag{4.5}$$

Hence we find the exact relation

$$\mu_{\text{eff}}^{tc}/\mu^{tc}(1) = \boldsymbol{\lambda}_{\text{eff}}/\lambda. \tag{4.6}$$

A similar relation was derived by Acrivos *et al.* [2], but their equation defining the mobility tensor differs from Eq. (4.4). Note that in general the mean temperature gradient $< \nabla T >$ differs from the applied uniform gradient $\nabla T_0 = \boldsymbol{g}_T$. Finally, we remark that the electrostatic version of Lorentz' reciprocity theorem [15, 16, 17] may be used to show that the effective thermal conductivity tensor $\boldsymbol{\lambda}_{\text{eff}}$ is symmetric.

5. Discussion

The theorem derived above applies only to the rather special case of a collection of equal-sized bubbles. Nonetheless it is of theoretical importance, since it provides a benchmark in the study of the more complicated situation of bubbles of different size, or more generally of a polydisperse suspension of fluid droplets with nonvanishing thermal conductivity and viscosity.

It has been shown by Acrivos *et al.* [2] that the problem of particles suspended in an electrolyte solution is mathematically identical to the thermocapillary problem considered above, provided the Debye length of the solution is much smaller than the particle radius. Hence for a set of equal-sized particles the derivation can be repeated with appropriate change of notation.

Note

* While this article was in print I was informed by Prof. A. Acrivos that the theorem derived above is contained in the paper Y. Wang, R. Mauri, and A. Acrivos, Thermocapillary migration of a bidisperse suspension of bubbles. J. Fluid Mech. 261 (1994) 47–64.

References

1. N.O. Young, J.S. Goldstein, and M.J. Block, The motion of bubbles in a vertical temperature gradient. *J. Fluid Mech.* 6 (1959) 350-356.
2. A. Acrivos, D.J. Jeffrey, and D.A. Saville, Particle migration in suspensions by thermocapillary or electrophoretic motion. *J. Fluid Mech.* 212 (1990) 95-110.
3. M. Meyyappan, W.R. Wilcox, and R.S. Subramanian, The slow axisymmetric motion of two bubbles in a thermal gradient. *J. Colloid Interface Sci.* 94 (1983) 243-257.
4. M. Meyyappan and R.S. Subramanian, The thermocapillary motion of two bubbles oriented arbitrarily with respect to a thermal gradient. *J. Colloid Interface Sci.* 97 (1984) 291-294.
5. J.L. Anderson, Droplet interactions in thermocapillary motion. *Intl. J. Multiphase Flow* 11 (1985) 813-824.
6. F. Feuillebois, Thermocapillary migration of two equal bubbles parallel to their line of centers. *J. Colloid Interface Sci.* 131 (1989) 267-274.
7. B.U. Felderhof, G.W. Ford, and E.G.D. Cohen, Cluster expansion for the dielectric constant of a polarizable suspension. *J. Stat. Phys.* 28 (1982) 135-164.
8. A.R. Edmonds, *Angular momentum in quantum mechanics*. Princeton: Princeton University Press (1974) 146 pp.
9. B. Cichocki, B.U. Felderhof, and R. Schmitz, Hydrodynamic interactions between two spherical particles. *Physico Chem. Hyd.* 10 (1988) 383-403.

10. R.F. Probstein, *Physicochemical Hydrodynamics*. Boston: Butterworths (1989) 353 pp.
11. R.S. Subramanian, The Stokes force on a droplet in an unbounded medium due to capillary effects. *J. Fluid Mech.* 153 (1985) 389-400.
12. R.B. Jones and R. Schmitz, Mobility matrix for arbitrary spherical particles in solution. *Physica* 149A (1988) 373-394.
13. B. Cichocki and B.U. Felderhof, Dielectric constant of polarizable, nonpolar fluids and suspensions. *J. Stat. Phys.* 53 (1988) 499-521.
14. K. Hinsen and B.U. Felderhof, Dielectric constant of a suspension of uniform spheres. *Phys. Rev.* B46 (1992) 12955-12963.
15. H.A. Lorentz, *Eene algemeene stelling omtrent de beweging eener vloeistof met wrijving en eenige daaruit afgeleide gevolgen.* Zittingsverslag Koninkl. Acad. van Wetensch. Amsterdam 5 (1896) 168–175.
16. H.A. Lorentz, Ein allgemeiner Satz, die Bewegung einer reibenden Flüssigkeit betreffend, nebst einigen Anwendungen desselben. In: H.A. Lorentz, *Abhandlungen über Theoretische Physik.* Leipzig: Verlag B.G. Teubner (1907) pp. 23-42.
17. H.A. Lorentz, A general theorem concerning the motion of a viscous fluid and a few consequences derived from it. In: H.A. Lorentz, *Collected Works*, Vol. IV. The Hague: Martinus Nijhoff Publishers (1937) pp. 7-14.