SELF-DIFFUSION OF DROPS IN A DILUTE SHEARED EMULSION

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ABSTRACT

Self-diffusion coefficients that describe cross-flow migration of nonBrownian drops in a dilute sheared emulsion were obtained by trajectory calculations. A boundary integral formulation was used to describe pairwise interactions between deformable drops; interactions between undeformed drops were described with mobility functions for spherical drops. The results indicate that drops have large anisotropic self-diffusivities which depend strongly on the drop viscosity and modestly on the shear-rate. Pairwise interactions between drops in shear-flow do not appreciably promote drop breakup.

INTRODUCTION

Shear-induced self-diffusion of nonBrownian drops in emulsions is important because it facilitates mixing. In the production of specialized polymer blends, macroscopic properties such as the mechanical strength rely on effective mixing of the emulsified melt to produce a uniform microstructure. In the absence of interfacial tension, the drop size in an efficient mixing device will continuously decrease until Brownian motion can effectively homogenize the fine droplets throughout the continuous phase.

However, interfacial tension places a lower bound on the drop size that can be obtained by mixing. For drops in shear-flow, significant deformation and breakup generally occur when the capillary number, $Ca = \dfrac{\mu \dot{\gamma} a}{\sigma}$ is $O(1)$, where $\dot{\gamma}$ is the imposed shear-rate, a is the undeformed drop radius, μ is the continuous-phase viscosity, and σ is the interfacial tension. The numerical value of the critical capillary number depends on the dispersed- to continuous-phase viscosity ratio, λ, and the dispersed-phase volume fraction, ϕ. For isolated drops with $0 < \lambda < 4$, the criterion $Ca = O(1)$ provides a reasonable estimate of the drop size produced by a given shear-rate (Hinch & Acrivos 1980; Grace 1982). The effect of drop interactions on the critical capillary number has not been studied thus the effect of volume fraction is unknown. Simple scaling arguments indicate that typical mixing operations generate nonBrownian deformable drops; thus, self-diffusion of deformable drops is an important mixing mechanism in most emulsification processes.

The $O(a)$ displacements and $O(\dot{\gamma}a)$ relative velocities between interacting particles or drops produce self-diffusivities that are $O(\dot{\gamma}a^2)$. Shear-induced self-diffusion of rigid spherical particles in has been experimentally observed (Eckstein et al. 1977; Leighton & Acrivos 1987) and numerically simulated (Brady & Bossis 1987). Pairwise interactions do not induce a net cross-flow displacement of smooth spheres; cross-flow self-diffusion results from multi-particle interactions. Wang et al. (1996) calculated the $O(\phi^2 \dot{\gamma}a^2)$ cross-flow self-diffusivity of smooth spheres in a sheared dilute suspension. Net cross-flow displacements can result from pairwise interactions between nonspherical particles or drops. Thus, nonspherical particles and drops have larger $O(\phi \dot{\gamma}a^2)$ self-diffusivities in dilute suspensions that result from pair interactions. da Cunha & Hinch (1996) computed the self-diffusivity of rough spheres in a dilute suspension but there have been no studies on the self-diffusion of drops.
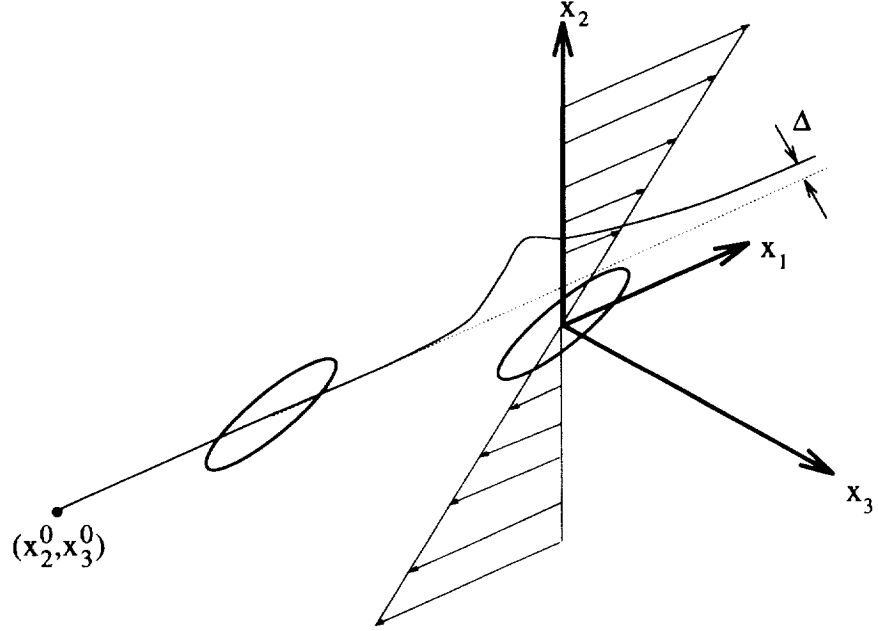
The aim of this article is to compute cross-flow self-diffusion coefficients of nonBrownian deformable drops in a sheared dilute emulsion. The effects of the capillary number and viscosity ratio were the focus

of our study. Neutrally buoyant drops, a monodisperse drop size distribution, and low Reynolds number conditions are assumed. Marangoni stresses on the drop interfaces that result from surfactant concentration gradients are neglected. The numerical procedure and numerical results are presented in the next two sections. Concluding remarks are made in the final section.

CALCULATION PROCEDURE

The nonsingular boundary integral formulation developed by Loewenberg & Hinch (1996) was used to compute the interactions and trajectories of deformable drops ($Ca > 0$) in shear-flow. For the limiting case $Ca \rightarrow 0$, spherical drop trajectories were obtained from Zinchenko (1983, 1984).

Figure 1: Schematic of relative trajectory between pair of deformable interacting drops in shear flow.

Self-diffusivities— The self-diffusion tensor is defined as half the rate-of-change of the random walk variance:

$$\mathbf{D} = \lim_{t \to \infty} \frac{1}{2}\frac{d}{dt}\langle \mathbf{\Delta}\mathbf{\Delta} \rangle \ , \tag{1}$$

where the cross-flow random walk displacement, $\mathbf{\Delta}$ has zero mean. The cross-flow displacement, $\mathbf{\Delta} = (\Delta_2, \Delta_3)$, is defined in fig. 1. For given values of Ca and λ, the cross-flow displacement of a drop resulting from its pairwise interaction with another identical drop depends on the initial offset of the drop trajectories, (x_2^0, x_3^0), at large separations in the flow direction, x_1. Only pairwise interactions between identical drops are considered on the assumption that the emulsion is dilute and monodisperse.

The rate of interactions that result in a particular cross-flow displacement, $\mathbf{\Delta}(x_2^0, x_3^0; Ca, \lambda)$, is $n \dot{\gamma} |x_2^0| \, dx_2^0 \, dx_3^0$, where n is the number density of drops: $\phi = \frac{4\pi}{3}a^3 n$. By definition (1), the dimensionless self-diffusion coefficient for drops in a dilute emulsion is (da Cunha & Hinch 1996):

$$f_\alpha(Ca, \lambda) = \frac{D_\alpha}{\phi\dot{\gamma}a^2} = \frac{3}{2\pi}\int_0^\infty\int_0^\infty \Delta_\alpha^2 x_2^0 \, dx_2^0 dx_3^0 \ , \tag{2}$$

where $\alpha = 2$ or 3 for cross-flow self-diffusion in the velocity gradient or the vorticity direction (cf. fig. 1). The result exploits the four-fold symmetry of integration in the $x_2^0 - x_3^0$ plane.

For deformable drops, the double integral of formula (2) was evaluated with about 1% error using 32 integrand evaluations (trajectory calculations) on a truncated square domain and extrapolating the result to infinity using the far-field form of the pair interaction (Kim & Karrila 1991). The calculations presented herein were obtained with a 4 × 4 domain. A comparison to the values obtained with an 8 × 8 domain indicated that the truncation error is 1-2%.
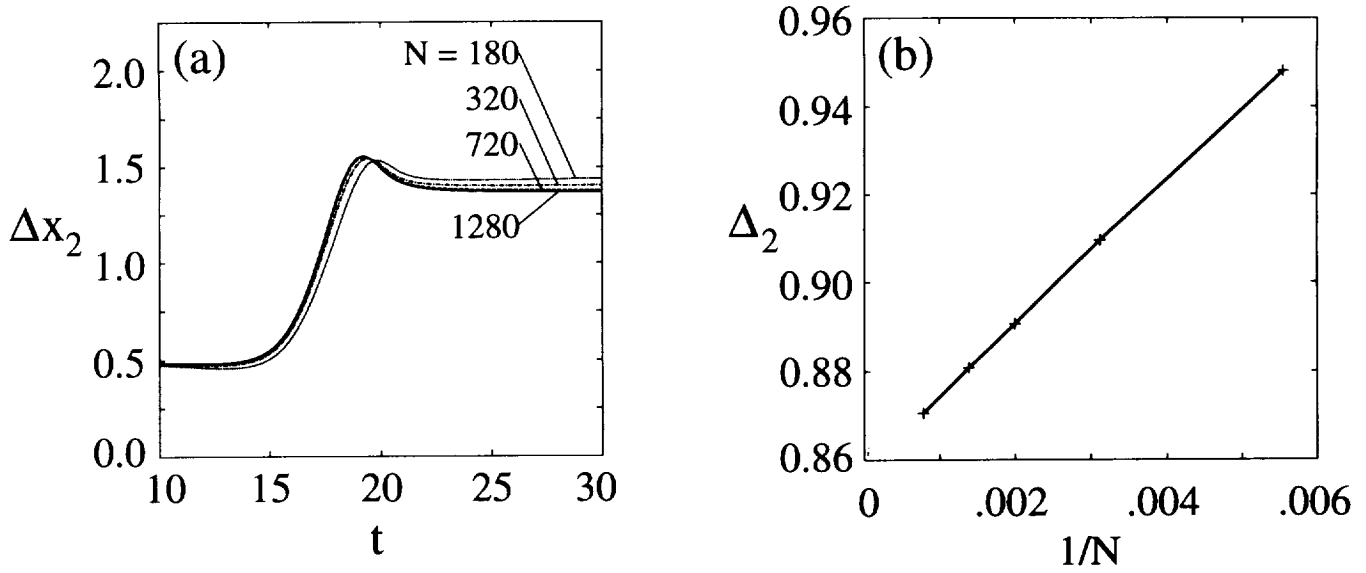
Figure 2: Relative trajectory of two interacting drops for $Ca = 0.3$, $\lambda = 1$; initially, one drop centered at origin and other drop at $(-10, 0.5, 0)$. a) Cross-flow separation (velocity gradient direction) versus time; results obtained obtained using $N = 180$ (dotted curve), 320 (dashed-dotted curve), 720 (dashed curve), and 1280 (solid curve) boundary elements. b) Cross-flow displacement versus reciprocal number of boundary elements, $1/N$.

Unstabilized hydrodynamically interacting spherical drops will coalesce for $R \leq 2E_{12}^{1/3}$, where $R = \sqrt{(x_2^0)^2 + (x_3^0)^2}$ is the magnitude of the initial trajectory offset and E_{12} is the "collision efficiency" (Wang et al. 1994). Herein, spherical drops were stabilized against coalescence by supplementing the hydrodynamic interaction with a singular, infintesimally short-range repulsion (Zinchenko 1984). For spherical drops with short-range repulsion, $\Delta(x_2^0, x_3^0)$ is nonzero only within the circular domain $R \leq 2E_{12}^{1/3}$. The mobility functions were tabulated for improved computational speed. For spherical drops formula (2) was evaluated with about 0.1% error using 1225 trajectory calculations.

Deformable drops can also be stabilized with a short-range repulsive interaction (Loewenberg & Hinch 1996) however, this was implemented only for $2 \leq \lambda \leq 5$ and for $\lambda < 0.1$ on the most closely-spaced trajectories ($R < 1$). Very small surface separations occur under these conditions. For $\lambda = 1$, we confirmed that the short-range repulsion had a negligible effect on the trajectories of deformable drops.

Cross-flow trajectory offsets were obtained with one drop initially centered at the origin and the second at a downstream location, $(-X_1, x_2^0, x_3^0)$. Trajectory integration was continued until the second drop passed the plane $x_1 = +X_1$. For deformable drops, the initial drop shapes corresponded to the stationary shapes of isolated drops under the same flow condtions. The error induced by trajectory truncation is $O(X_1^{-3})$ (Kim & Karrila 1991). We used $X_1 = 8$ for deformable drops and $X_1 = 20$ for spherical drops. Based on a limited number of calculations with larger values of X_1, we estimate that trajectory truncation error is about 1% for deformable drops and about 0.1% for spherical drops.

Computation Time and Numerical Convergence— For deformable drops with $Ca = 0.3$ and $\lambda = 1$, self-diffusivities were obtained in 2 hours on a workstation using $N = 720$ boundary elements. The calculations are 3-4 times slower for $\lambda \neq 1$ because an iterative solution of the integral equation is required.

The results depicted in fig. 2 demonstrate numerical convergence of the boundary integral calculations for trajectories of deformable drops. Fig. 2b demonstrates that the total discretization error resulting from
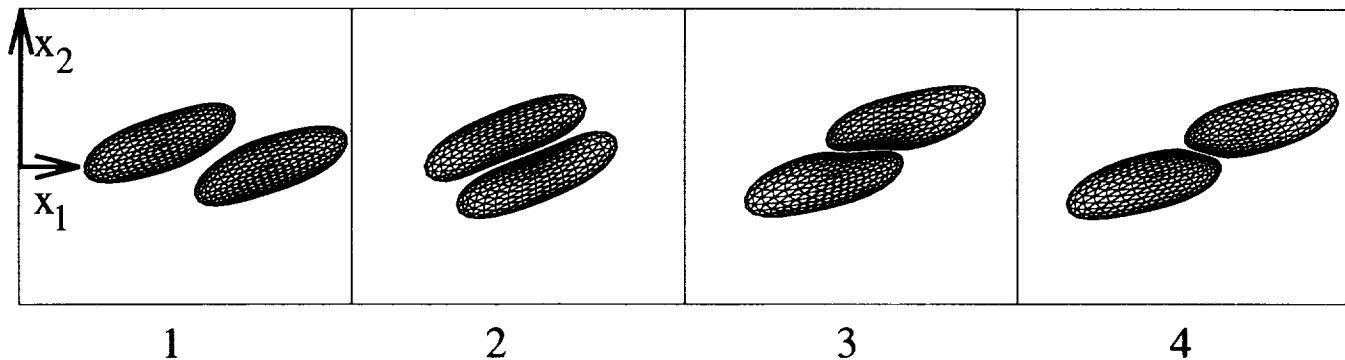
Figure 3: Sequences (1-4) showing the interaction between two drops in shear flow with $Ca = 0.4$, $\lambda = 1$. Initially, one drop centered at origin and other drop at (-10, 0.5, 0).

the curvature calculation, surface integration, and trajectory integration is $O(N^{-1})$. Herein, self-diffusivities were computed with $N = 720$ thus, discretization errors are about 2% which is comparable to the remaining sources of error discussed above.

Self-diffusivities for spherical drops require less than a minute of CPU time and are accurate to about 0.1%.

NUMERICAL RESULTS

Drop Breakup—An example of a pair interaction between deformable drops in shear-flow is depicted in fig. 3. The critical capillary number for breakup of an isolated drop in shear flow is lowest for $\lambda \approx 1$; for $\lambda = 1$, $Ca \simeq 0.41$ is critical (Rallison 1981). The trajectory depicted in fig. 3 demonstrates that even for capillary numbers very close to critical, strong pairwise interactions do not result in drop breakup. Other calculations with $\lambda \neq 1$ also showed no tendency for interaction-enhanced breakup. Apparently pairwise drop interactions do not induce significantly subcritical capillary number breakup. Thus, the critical capillary number is a weak function of volume fraction at least in dilute emulsions.

In part, breakup is averted because of the reduced cross-section for interaction between highly deformed drops. Breakup requires enhanced drop elongation but a detailed inspection of the numerical results revealed that the extra deformation induced by a pairwise interaction tends to deform drops in the x_3—direction. Deformable drops can easily squeeze past each other which tends to prevent breakup.

Self-diffusivities— Figs. 4 and 5 depict self-diffusivities as functions of shear-rate (capillary number) and viscosity ratio. Self-diffusion is only a moderate function of capillary number; figs. 4 and 5 show that self-diffusivities vary by a factor of about 2 as the capillary number is varied over a wide range. By contrast, self-diffusivities are a strong function of viscosity ratio.

Anisotropic self-diffusion results from the bias of trajectory displacements in the velocity gradient direction. Self-diffusion in the velocity gradient direction, f_2 is much larger than self-diffusion in the vorticity direction, f_3. For stabilized spherical bubbles ($\lambda = 0$), it can be shown that the ratio f_2/f_3 is exactly 2. For deformable bubbles with $Ca = 0.3$, $f_2/f_3 \simeq 6$. Fig. 5 indicates that anisotropy increases with viscosity ratio; $f_2/f_3 > 20$ for $\lambda \geq 10$.

For $\lambda = 10$, f_2 and f_3 are approximately equal to the self-diffusivities predicted for spherical particles with 3% roughness (da Cunha & Hinch 1996). For $\lambda < 10$, drop diffusivities are considerably larger than the values for rough spherical particles.

As expected, self-diffusivities vanish for large λ because $D = O(\phi^2)$ for smooth spheres (Wang et al. 1996). The results depicted in fig. 5 indicate that self-diffusion becomes insensitive to capillary number
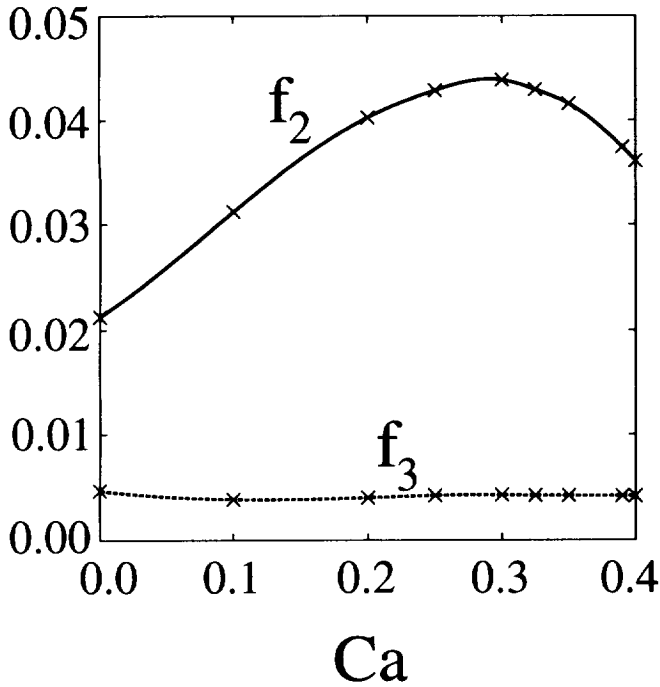
Figure 4: Self-diffusion coefficients as a function of capillary number for $\lambda = 1$; solid curve: diffusion parallel to velocity gradient, f_2; dashed curve: diffusion parallel to vorticity, f_3.
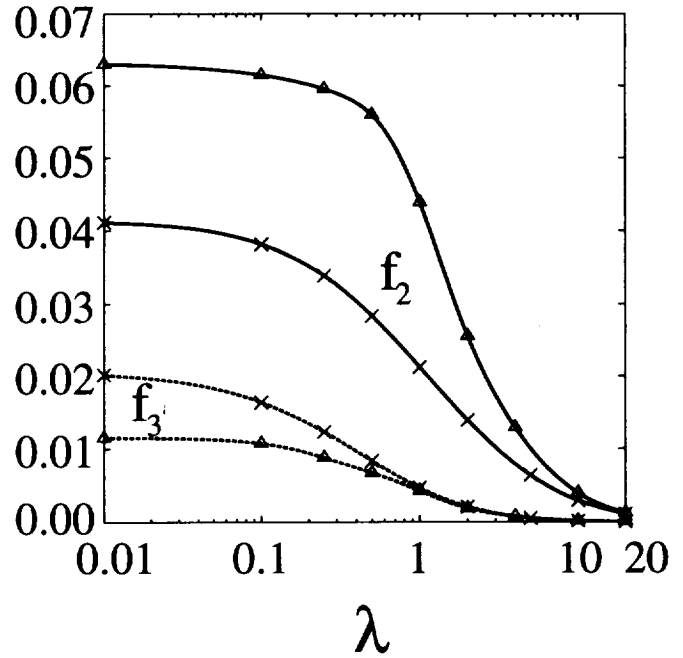
Figure 5: Self-diffusion coefficients as a function of viscosity ratio for $Ca = 0.3$ ($\triangle$) and $Ca = 0$ ($\times$); solid curves: diffusion parallel to velocity gradient, f_2; dashed curves: diffusion parallel to vorticity, f_3.

for large viscosity ratios. Closer inspection of the numerical results indicates that self-diffusivities vanish exponentially for $\lambda \gg 1$.

Fig. 4 shows that f_2 exhibits a maximum which may result from a balance between the increase of far-field ($R > 2$) trajectory displacements with drop deformation and the decrease of near-field trajectory displacements with reduced drop cross-section. Under the same conditions, f_3 is essentially independent of Ca. Fig. 4 shows a smooth transition from results for $Ca \geq 0.1$ to the results for $Ca = 0$ that were obtained using spherical drops stabilized against coalescence by a short-range singular repulsion.

CONCLUSIONS

Cross-flow self-diffusivities have been computed for drops in a dilute emulsion. The results show that self-diffusivities depend strongly on the viscosity ratio and moderately on the capillary number. Self-diffusivities are much larger in the velocity gradient direction than in the vorticity direction. Drops have large self-diffusivities compared to rigid spherical particles.

The interactions between deformable drops were described with boundary intergral calculations; $O(1/N)$ numerical convergence was obtained, where N is the number of boundary elements. Mobility functions for spherical drops were used to describe the interactions between drops in the zero deformation limit.

The calculations also indicate that drop interactions do not induce significantly subcritical capillary number breakup. In dilute emulsions, the critical capillary number is a weak function of volume fraction because deformable drops can easily squeeze past each other.

ACKNOWLEDGEMENTS

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