Mutual Diffusion of Inclusions in Freely Suspended Smectic Liquid Crystal Films

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We study experimentally and theoretically the hydrodynamic interaction of pairs of circular inclusions in two-dimensional, fluid smectic membranes suspended in air. By analyzing their Brownian motion, we find that the radial mutual mobilities of identical inclusions are independent of their size but that the angular coupling becomes strongly size dependent when their radius exceeds a characteristic hydrodynamic length. These observations are described well for arbitrary inclusion separations by a model that generalizes the Levine-MacKintosh theory of point-force response functions and uses a boundary-element approach to calculate the mobility matrix for inclusions of finite extent.

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Since many of the processes critical for the life of the cell take place in the plasma membrane or in the membranes of organelles, the physics of transport, diffusion, and aggregation of particles in thin, fluid membranes is of fundamental interest. Biological membranes are typically crowded, being populated by a high density of mutually hydrodynamically interacting proteins or protein assemblies. A key feature of the hydrodynamic interactions between such particles is that they are, in general, mediated both by the membrane and by the surrounding fluid. In this Letter, we develop the theoretical tools for analyzing the collective hydrodynamics of multiple inclusions in two-dimensional (2D) fluid membranes and test this modeling approach in high-precision experiments on inclusions in freely suspended smectic liquid crystal films.

Saffman and Delbrück (SD) studied theoretically the mobility of a single particle of radius a in a fluid layer of viscosity η and thickness h embedded in a different fluid of viscosity η' and found that the mobility of the inclusions depends on the Saffman length $\ell_S = \eta h/(2\eta')$ [1]. The general dependence of mobility on size and the crossover from three-dimensional (3D) to 2D behavior as the particle size is reduced was subsequently derived by Hughes-Pailthorpe-White (HPW) [2].

Since it is difficult to measure viscosity and to vary the length scales a and ℓ_S systematically over a wide range in biomembranes, the SD and HPW theories have not been extensively tested in biological systems. In thin, fluid smectic films, however, the relevant physical parameters are known and can be readily varied. The Saffman length in these systems is tens of microns, comparable to ℓ_S in biological membranes with high viscosity [3]. Nguyen *et al.* [4] previously demonstrated the crossover behavior predicted by HPW theory by measuring the Brownian diffusion of isolated inclusions in smectic films. The hydrodynamic description of several inclusions in a fluid membrane is complex because their mobilities depend not only on their size and the drag from the surrounding fluid(s) but also on the hydrodynamic interactions between them, so such systems are much less well studied. Bussell *et al.* [5] extended SD theory in order to predict the mobilities of two cylinders in a membrane in the limit $a \ll \ell_S$. Levine and MacKintosh (LM) derived the response function for a point force in a 2D fluid [6] (see also [1]), an approach to computing the mobility matrix in the far-field limit that forms the basis of the generalized hydrodynamic model presented below.

Microrheology experiments have been carried out previously on several model membrane systems. For example, Cheung *et al.* measured the diffusion of colloidal particles embedded in soap films and showed that their long-range hydrodynamic interactions were 2D in nature [7]. Di Leonardo *et al.* used laser tweezers to manipulate colloidal particles in thick soap films in order to determine their mutual 2D eigenmobilities in the limit of large Saffman lengths [8]. In an earlier study, Prasad *et al.* probed experimentally the correlated motion of colloidal particles at the air-water interface [9]. In their analysis, they assumed that the particles were sufficiently dilute that they could be treated as points. One may ask under what circumstances the far-field approximation is justified and to what extent the Levine-MacKintosh model remains valid, for inclusions of finite size that are close together. Our experiments on smectic films reveal that, in many cases, the mutual mobilities of large circular inclusions of the same radius are well described by the LM theory. Surprisingly, the radial mobility, which describes the relative motion of two inclusions toward or away from each other, is found to be independent of inclusion size, even when the inclusions are very near each other, an observation confirmed by our extended hydrodynamic model.

In this Letter, we report measurements and theoretical modeling of the mobilities of pairs of inclusions in smectic A liquid crystal films, fluid membranes that are only a few nanometers thick. These films are very stable [10] and provide an ideal platform for studying hydrodynamics in 2D fluids [11–14]. In our experiments, we observe the Brownian motion of silicone oil droplets and smectic "islands" embedded in the films. The islands are disk shaped, thicker regions of the film bounded by edge dislocations [Figs. 1(a), 1(b)] that can be created with diameters of between a few and several hundred μm [4].

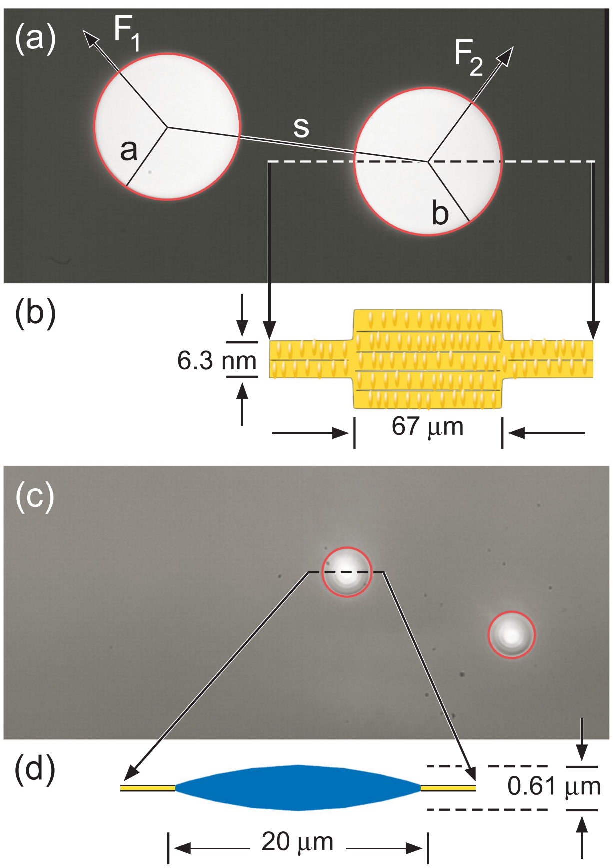

FIG. 1 (color online). Island and silicone oil droplet pairs in thin 8CB films viewed in reflection. (a) Islands with radii a and b and separation s subject to forces F_1 and F_2. (b) Schematic cross section of a five-layer island in a two-layer film (not to scale). (c) Silicone oil droplets in a six-layer film. (d) Cross section of a typical silicone oil inclusion (drawn with expanded vertical scale), measured using optical interference in monochromatic light [15].

The oil droplets form lens-shaped rather than flat inclusions [Figs. 1(c), 1(d)]. They are essentially insoluble in liquid crystal, and their sizes remain practically constant over long time intervals. This is particularly useful for making mobility measurements of very small inclusions because smectic islands less than about 10 μm in diameter tend to shrink rapidly and vanish within a few minutes, whereas silicone oil droplets of similar size remain practically unchanged for half an hour or more.

The liquid crystal used in our experiments is 8CB (4′-n-octyl-4′-cyanobiphenyl, Sigma-Aldrich), a room-temperature smectic A material. The density and viscosity of 8CB are $\rho \approx 0.96\ \mathrm{g/cm^3}$ [16] and $\eta = 0.052$ Pa s [13], respectively, while the viscosity of ambient air is $\eta' = 1.827 \times 10^{-5}$ Pa s [17]. Each smectic layer has a thickness of 3.17 nm [18]. Freely suspended films from two to six molecular layers thick, corresponding to Saffman lengths between 9 and 27 μm, were formed by spreading a small amount of the liquid crystal across a 5 mm-diameter hole in a glass cover slip and were then observed using reflected light microscopy. Immediately after a film is drawn, one typically observes many islands, with a range of diameters. The film may then be gently sheared using an air jet to break larger islands into smaller ones for study. To create oil droplets, the LC film was put into a sealed chamber, where it was left until it was uniform in thickness. A double-sealed rotary pump (Welch Model 1400) was then used to reduce the chamber pressure to 3×10^{-3} Torr. After about an hour, a small amount of vaporized pump oil has made its way to the film chamber, where it eventually condenses onto the film and forms visible droplets with diameters of between 4 and 15 μm. We then restore the chamber to atmospheric pressure and observe the diffusion behavior of the droplets. Isolated pairs of islands (or oil droplets) of similar sizes and far from other inclusions and the film boundaries were selected for study.

The films are carefully leveled to minimize any gravitational drift, allowing us to record, with high spatial resolution at a typical video frame rate of 24 fps, the motion of inclusion pairs for several minutes before they diffuse out of the field of view. We use Canny's method for edge detection [19] and Taubin's curve fitting algorithm [20] to measure accurately the positions and sizes of the inclusions in each frame. The effects of any overall drift are removed analytically from the resulting trajectories [4]. The film thickness, an integral number of smectic layers, is determined precisely by comparing the reflectivity of the film with black glass [21].

In order to model the effects of the long-range hydrodynamic interactions between the inclusions, we consider two circular domains of radii a and b that are subjected to external forces $\mathbf{F}_1$ and $\mathbf{F}_2$, respectively. Since we are in the low Reynolds number regime, inertial effects are unimportant and the hydrodynamics can be described using the Stokes equations [22]. The velocity of each inclusion is a linear function of the applied forces, that of the first inclusion, for example, being given by

$$\mathbf{V}_1 = \mathbf{M}_{11}\mathbf{F}_1 + \mathbf{M}_{12}\mathbf{F}_2, \tag{1}$$

where $\mathbf{M}_{11}$ is the self-mobility matrix and $\mathbf{M}_{12}$ is the mutual mobility matrix. Since a pair of circular inclusions has mirror symmetry about the line connecting their centers, the only nonvanishing components of the mobility matrices are the diagonal elements M_{11}^{rr}, $M_{11}^{\theta\theta}$, M_{12}^{rr}, and $M_{12}^{\theta\theta}$ [23], where rr refers to the radial motion of the inclusions (along the line connecting their centers) and $\theta\theta$ refers to tangential motion (perpendicular to this line). The mutual mobilities can be extracted from the experimental measurements by computing the cross-correlation function [24]

$$\langle \Delta\mathbf{r}_1(t)\cdot\Delta\mathbf{r}_2(t)\delta(r_{12}(0)-s)\rangle = 2k_BT(M_{12}^{rr}(s)+M_{12}^{\theta\theta}(s))t, \tag{2}$$

where $\Delta\mathbf{r}_k(t) = \mathbf{r}_k(t) - \mathbf{r}_k(0)$ is the displacement of the kth inclusion in time interval t and $r_{12}(0)$ and s are respectively the distances between the centers of the inclusions at $t = 0$ and at time t [see Fig. 1(a)].

The observed dependence of the mutual mobilities M_{12}^{rr} and $M_{12}^{\theta\theta}$ (scaled by $4\pi\eta h$) on the dimensionless center-to-center distance s/ℓ_S is plotted in Fig. 2 for pairs of oil drops with approximately equal radii $a \approx b < \ell_S$. Remarkably, in this 2D regime, where dissipation occurs primarily in the smectic film [25], both mutual mobilities are found to be independent of the inclusion size. In the LM theory, $\alpha^{\alpha\beta}$ gives the flow induced by a point force at $\mathbf{x}: v^\alpha(\mathbf{x}') = \alpha^{\alpha\beta}(\mathbf{x}'-\mathbf{x})f^\beta\delta(\mathbf{x})$. Since the LM model describes the microrheology of viscoelastic membranes and we treat the smectic films as purely viscous 2D fluids, we use an $\boldsymbol{\alpha}$ corresponding to $-i\omega\alpha$ in the LM theory. The response function $\alpha^{\alpha\beta}$ may be split into parallel (radial) and perpendicular (tangential) contributions $\alpha^{\alpha\beta}(\mathbf{x}) = \alpha_\parallel(z)\hat{x}^\alpha\hat{x}^\beta + \alpha_\perp(z)[\delta^{\alpha\beta} - \hat{x}^\alpha\hat{x}^\beta]$, where $z = |\mathbf{x}|/\ell_S$. Both $\alpha_\parallel(z)$ and $\alpha_\perp(z)$ diverge logarithmically as $z \to 0$, and for large z we have $\alpha_\parallel(z) \sim 1/z$ and $\alpha_\perp(z) \sim 1/z^2$. Even when the drop separation s is comparable to or smaller than the Saffman length, M_{12}^{rr} and $M_{12}^{\theta\theta}$ closely follow the $\alpha_\parallel$ and $\alpha_\perp$ components of the LM response function tensor $\alpha^{\alpha\beta}$ (black dashed lines in Fig. 2) [6].

Now we consider large smectic islands with $a \approx b > \ell_S$, the 3D hydrodynamic regime in which dissipation occurs primarily in the air surrounding the smectic film. Surprisingly, here too the observed radial mutual mobility M_{12}^{rr} is described well by the LM response function $\alpha_\parallel$ for pointlike particles, even when the inclusions are very close together [Fig. 3(a)]. The tangential mutual mobilities $M_{12}^{\theta\theta}$, however, deviate significantly from $\alpha_\perp$ and depend strongly on radius [Fig. 3(b)].

These experimental observations motivated us to extend the LM model beyond the far-field approximation

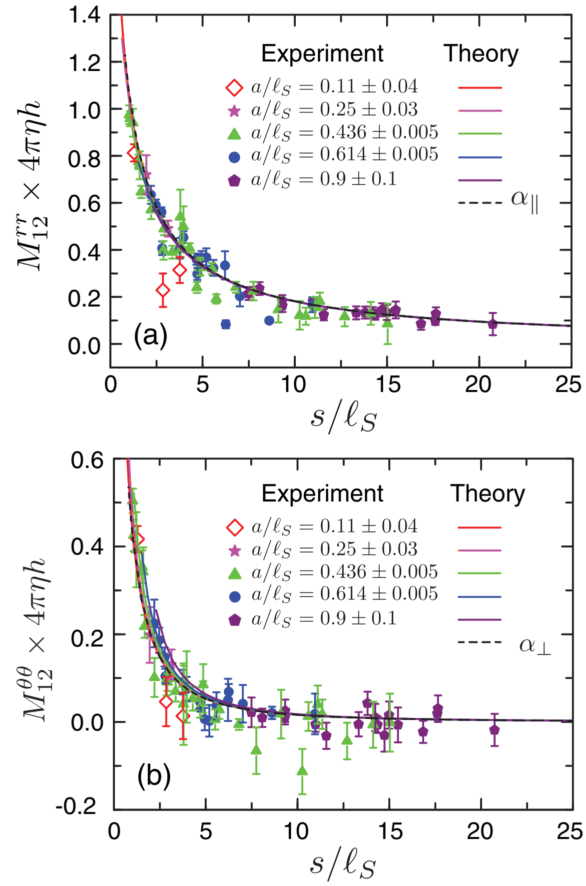

FIG. 2 (color online). Measured and predicted mutual mobilities (a) M_{12}^{rr} (radial) and (b) $M_{12}^{\theta\theta}$ (tangential) of pairs of oil droplets with radii $a \approx b < \ell_S$ in smectic membranes, as a function of dimensionless separation s/ℓ_S. The statistical uncertainties here and in Fig. 3 are a consequence of combining measurements on several pairs of inclusions of the same average size. The LM response functions $\alpha_\parallel$ and $\alpha_\perp$ are shown as dashed curves.

in order to be able to characterize the interactions of circular inclusions of arbitrary radius and separation. In our theoretical approach, we utilize a boundary element method in which the flow field in the film generated by the motion of an inclusion of radius a is determined by integrating the effects of an array of point forces along the inclusion boundary,

$$v^\alpha(\mathbf{x}') = \sum_{j=1,2}\int_0^{2\pi} d\phi f_j^\beta(\phi)\alpha^{\alpha\beta}(\mathbf{x}'-\mathbf{x}_j(\phi)). \tag{3}$$

Here $\alpha, \beta = x, y$, $j = 1, 2$ labels the inclusion, $f_j^\beta(\phi)$ are the (initially unknown) strengths of the point forces, and $\alpha^{\alpha\beta}$ is the LM response function. The force densities $f_j^\beta(\phi)$ are found by demanding no-slip boundary conditions $v^\alpha = V_j^\alpha$ at each inclusion and numerically solving Eq. (3). In the particular case of two inclusions of equal radius, moving with velocities V and subject to forces of equal magnitude F, one may determine the self- and mutual mobilities by

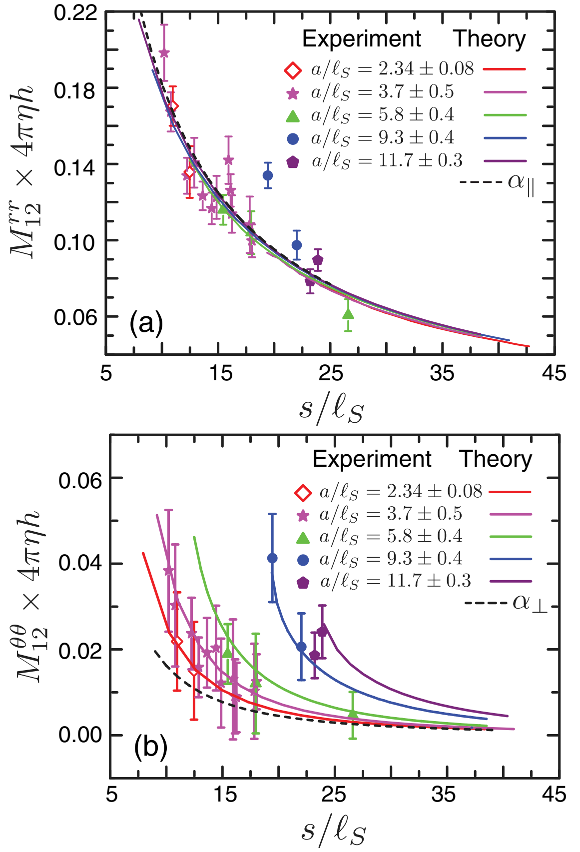

FIG. 3 (color online). Measured and predicted mutual mobilities (a) M_{12}^{rr} (radial) and (b) $M_{12}^{\theta\theta}$ (tangential) of pairs of islands with radii $a \approx b > \ell_S$ in smectic membranes, as a function of dimensionless separation s/ℓ_S. The LM response functions $\alpha_\parallel$ and $\alpha_\perp$ are shown as dashed curves.

invoking the linearity of the governing equations (Eq. (1) and considering inclusion motions symmetric and antisymmetric in x and y illustrated in the Supplemental Material [26]. The calculations will be described in full detail elsewhere [27].

The mutual mobilities obtained in this way (solid curves in Figs. 2 and 3) match the experimental data well for all experimentally accessible inclusion sizes and ratios of a/ℓ_S. The model predicts, furthermore, that the self-mobilities M_{kk}^{rr} and $M_{kk}^{\theta\theta}$ also depend on the distance between the inclusions, being reduced when another inclusion is nearby, but this is a relatively weak effect that is difficult to measure in our experiments. In addition, we note that when applied to calculating the self-mobility of isolated inclusions with radii in the range $0.1\ell_S < a < 10\ell_S$, our model reproduces the HPW predictions [2] very well, confirming that accurate results can be obtained by assuming that the inclusions are rigid [4], ignoring their interiors and modeling the total force on each inclusion as the superposition of the forces along its circumference.

The observation that the mutual radial mobility of two identical circular inclusions is size independent, even at small separations, may be understood by considering the 2D velocity field around a single inclusion moving in a membrane, computed as described above for both small and large values of a/ℓ_S and shown in Fig. 4. For all values of a/ℓ_S, the flow fore and aft of the inclusion falls off more slowly with radial distance than the flow in the regions beside the inclusion [6], the precise form of the fall off depending on the value of a/ℓ_S (Supplemental Material [26]). The velocity gradients across the flow field in the fore and aft regions are relatively small in all cases, implying that a finite-sized second inclusion experiences the same mean flow as a pointlike inclusion when the two inclusions move towards or away from each other [Figs. 2(a) and 3(a)]. Furthermore, a multipole expansion of the computed velocity field (Supplemental Material [26]) shows that the contributions of the higher-order multipoles to the radial mutual mobility become small when the point forces are distributed uniformly and in a mirror-symmetric way along the circumference of the (circular) inclusion, explaining why the LM response functions describe the radial mutual mobility accurately.

A similar argument holds for the tangential relative motion when the Saffman length is large [Figs. 2(b) and 4(a)], but in the case of small Saffman lengths [Figs. 3(b) and 4(b)], there are significant velocity gradients in the regions directly to either side of the inclusion that result in a strong size dependence of the mutual mobility. In this case, the higher-order multipole contributions to the tangential mobility can not be neglected, even for a symmetric distribution of point forces.

Finally, when the inclusions have different diameters, the radial mutual mobility is found experimentally to be size dependent at all Saffman lengths. The model confirms this result and predicts similar deviations from the point-source approximation when the inclusions are not circular, for example, when they are elliptical.

In summary, we have probed the hydrodynamic interactions of a pair of inclusions in a thin fluid membrane. A theory generalizing the point particle approach of Levine and MacKintosh in order to consider inclusions of finite extent and arbitrary separation reproduces the experimental

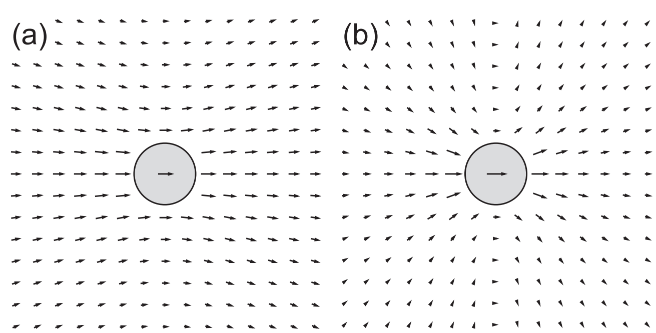

FIG. 4. Model flow fields near moving circular inclusions of radius (a) $a/\ell_S = 0.1$ and (b) $a/\ell_S = 10$ in a 2D membrane.

mobilities obtained by measuring the Brownian motion of oil droplets and islands in thin smectic A liquid crystal films. The model confirms the surprising experimental observation that for identical circular inclusions, the mutual radial mobilities are independent of size for all Saffman lengths, while the mutual tangential mobilities depend strongly on both size and separation only when the inclusions are larger than the Saffman length.

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[1] P. G. Saffman and M. Delbrück, Proc. Natl. Acad. Sci. U.S.A. **72**, 3111 (1975); P. G. Saffman, J. Fluid Mech. **73**, 593 (1976).
[2] B. D. Hughes, B. A. Pailthorpe, and L. R. White, J. Fluid Mech. **110**, 349 (1981).
[3] P. Cicuta, S. L. Keller, and S. L. Veatch, J. Phys. Chem. B **111**, 3328 (2007).
[4] Z. H. Nguyen, M. Atkinson, C. S. Park, J. Maclennan, M. Glaser, and N. Clark, Phys. Rev. Lett. **105**, 268304 (2010).
[5] S. J. Bussell, D. L. Koch, and D. A. Hammer, J. Fluid Mech. **243**, 679 (1992).
[6] A. J. Levine and F. C. MacKintosh, Phys. Rev. E **66**, 061606 (2002).
[7] C. Cheung, Y. H. Hwang, X.-l. Wu, and H. J. Choi, Phys. Rev. Lett. **76**, 2531 (1996).
[8] R. Di Leonardo, S. Keen, F. Ianni, J. Leach, M. J. Padgett, and G. Ruocco, Phys. Rev. E **78**, 031406 (2008).
[9] V. Prasad, S. A. Koehler, and E. R. Weeks, Phys. Rev. Lett. **97**, 176001 (2006).
[10] C. Y. Young, R. Pindak, N. A. Clark, and R. B. Meyer, Phys. Rev. Lett. **40**, 773 (1978).
[11] C. D. Muzny and N. A. Clark, Phys. Rev. Lett. **68**, 804 (1992).
[12] J. C. Geminard, R. Holyst, and P. Oswald, Phys. Rev. Lett. **78**, 1924 (1997).
[13] F. Schneider, Phys. Rev. E **74**, 021709 (2006).
[14] A. Eremin, S. Baumgarten, K. Harth, R. Stannarius, Z. H. Nguyen, A. Goldfain, C. S. Park, J. E. Maclennan, M. A. Glaser, and N. A. Clark, Phys. Rev. Lett. **107**, 268301 (2011).
[15] H. Schüring and R. Stannarius, Langmuir **18**, 9735 (2002).
[16] A. J. Leadbetter, J. L. A. Durrant, and M. Rugman, Mol. Cryst. Liq. Cryst. **34**, 231 (1976).
[17] *Handbook of Chemistry and Physics*, 54th ed., edited by R. C. Weast (CRC Press, Cleveland, 1973–1974).
[18] D. Davidov, C. R. Safinya, M. Kaplan, S. S. Dana, R. Schaetzing, R. J. Birgeneau, and J. D. Litster, Phys. Rev. B **19**, 1657 (1979).
[19] J. Canny, *IEEE Transactions on Pattern Analysis and Machine Intelligence* (IEEE, New York, 1986), Vol. 8, pp. 679–698.
[20] G. Taubin, *IEEE Transactions on Pattern Analysis and Machine Intelligence* (IEEE, New York, 1991), Vol. 13, pp. 1115—1138.
[21] C. Rosenblatt and N. M. Amer, Appl. Phys. Lett. **36**, 432 (1980).
[22] For even the most rapidly moving inclusions in our experiments, for which $v \sim 1\ \mu\mathrm{m/s}$, both $Re = \rho v a/\eta \ll 1$ and $Re' = \rho' v a/\eta' \ll 1$, where ρ' is the density of air.
[23] S. Kim and J. S. Karrila, *Microhydrodynamics: Principles and Selected Applications* (Butterworth-Heinemann, Boston, MA, 1991).
[24] J. C. Crocker, M. T. Valentine, E. R. Weeks, T. Gisler, P. D. Kaplan, A. G. Yodh, and D. A. Weitz, Phys. Rev. Lett. **85**, 888 (2000).
[25] H. A. Stone, J. Fluid Mech. **645**, 1 (2010).
[26] See the Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.113.128304 for a description of the method used to calculate the mutual diffusion of inclusions of arbitrary shape and size and a discussion of the multipole expansion of the velocity field.
[27] T. Kuriabova *et al.* (to be published).