Unsteady motion of a perfectly slipping sphere

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An integral expression for the translational velocity of a perfectly slipping spherical particle under a time-dependent applied force in unsteady Stokes flow is derived. For example, when the ratio of particle density to fluid density is small, our analysis pertains to an inviscid bubble in a viscous fluid. We determine an explicit form of the particle velocity under an impulsive force, wherefrom the velocity autocorrelation function and mean-squared displacement of a perfectly slipping sphere undergoing Brownian motion are obtained. The above results are contrasted against the time-dependent diffusion of a rigid sphere with no hydrodynamic slip. Finally, the thermal force power spectral density is analytically calculated for a diffusing sphere with arbitrary slip length. We suggest this quantity to be suitable to infer slip length from the measurement of nondiffusive Brownian motion.

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I. INTRODUCTION

Modeling the unsteady motion of small objects in a viscous fluid is relevant to contaminant dispersion [1], particle clustering in turbulence [2], micro-organism movement [3], and electrophoresis [4]. The motion of a rigid sphere to which fluid perfectly adheres (i.e., the no-slip condition is obeyed) is described at zero Reynolds number by the so-called Basset-Boussinesq-Oseen (BBO) equation [5]

$$\frac{4}{3}\pi a^3\rho_b\frac{d\boldsymbol{U}(t)}{dt} = -6\pi\mu a\boldsymbol{U}(t) - \frac{2}{3}\pi\rho a^3\frac{d\boldsymbol{U}(t)}{dt} - \int_{-\infty}^{t} K(t-t')\frac{d\boldsymbol{U}(t')}{dt'}\,dt' + \boldsymbol{F}_A(t), \quad (1)$$

where

$$K(t) = \begin{cases} \frac{6\pi\mu a^2}{\sqrt{\pi t\nu}} & \text{for } t \geqslant 0, \\ 0 & \text{for } t < 0. \end{cases} \quad (2)$$

In (1) and (2), a is the particle radius, ρ_b is the particle density, ρ is the fluid density, μ is the dynamic viscosity and $\nu = \mu/\rho$ is the kinematic viscosity, $\boldsymbol{U}(t)$ is the particle velocity, t is time, and $\boldsymbol{F}_A(t)$ is an externally applied force. The BBO equation is just Newton's second law of motion for the particle. The left-hand side in (1) is the particle inertia, which is balanced by the hydrodynamic force (the first three terms on the right-hand side) and the applied force. The first term on the right-hand side is the quasisteady Stokes drag. The next two terms originate from unsteady effects in the flow. The second term on the right-hand side is the acceleration reaction on the particle due to the inviscid pressure disturbance caused by its changing velocity. The Basset history force is described by the integral expression in (1) and originates from the diffusion of vorticity away from the particle. The memory kernel $K(t)$ acts to weigh the importance of the history of the particle motion $d\boldsymbol{U}(t)/dt$ on its current velocity.

The BBO equation is a first-order integrodifferential equation for the time-dependent velocity of a spherical, no-slip particle under an arbitrary time-dependent force. Due to the nonlocal nature of the Basset force, numerical solutions are generally sought out, as analytical solutions can be obtained only for sufficiently simple forms of $\boldsymbol{F}_A(t)$. Numerical difficulties in solving (1) are due to the history integral: $K(t)$ is integrably singular as $t \to 0$, and the integration must be calculated throughout the entire history of motion, which presents storage issues [1]. The generalization of the BBO equation to account for ambient flows is known as the Maxey-Riley (MR) equation, which is a nonlinear equation, since the instantaneous force on the particle depends on its position in the flow, which is unknown *a priori* [6].

While there has been much work on how rigid, no-slip spherical particles are transported in unsteady flows, there is a lack of comparative knowledge for bubbles, drops, and slipping spheres. The key difference is that a rigid sphere is subject to the no-slip boundary condition, while the surface of a drop or bubble is mobile and a slipping sphere admits hydrodynamic slip. The equivalent to the BBO equation for a perfectly slipping sphere is [7]

$$\frac{4}{3}\pi a^3\rho_b\frac{d\boldsymbol{U}(t)}{dt} = -4\pi\mu a\boldsymbol{U}(t) - \frac{2}{3}\pi\rho a^3\frac{d\boldsymbol{U}(t)}{dt} - \int_{-\infty}^{t} G(t-t')\frac{d\boldsymbol{U}(t')}{dt'}\,dt' + \boldsymbol{F}_A(t), \quad (3)$$

where

$$G(t) = \begin{cases} 8\pi\mu a\, e^{9t\nu/a^2}\,\mathrm{erfc}(3\sqrt{t\nu/a^2}) & \text{for } t \geqslant 0, \\ 0 & \text{for } t < 0. \end{cases} \quad (4)$$

Note, by "perfectly slipping" we mean that the surface of the sphere cannot support a shear stress. Here, erfc is the complementary error function. The memory kernel $G(t)$ is different from that of a no-slip sphere: It is bounded as $t \to 0$,

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while $K(t)$ is unbounded. Note, both $G(t)$ and $K(t)$ decay as $t^{-1/2}$ as $t \to \infty$. Thus, we expect significant differences in the particle motion on times small compared to the momentum diffusion time a^2/ν. For a particle with radius $a = 1\ \mu$m in water with kinematic viscosity $\nu = 10^{-6}$ m^2/s, we have $a^2/\nu \approx 10^{-6}$ s. Thus, these differences would be important for particle motion on the microsecond timescale, or actuated by external forces that vary at frequencies of O(MHz). For $\rho_b/\rho \to 0$, (3) corresponds to an inviscid bubble [8], and for $\rho_b/\rho = 1$, (3) corresponds to a neutrally buoyant sphere with perfect slip [9].

In this article, we calculate the time-dependent velocity of a perfectly slipping sphere under an arbitrary applied force. That is, we will invert (3) to determine an integral expression for the time-dependent velocity in terms of the history of the applied force. We derive an explicit expression for the time-dependent velocity under a force impulse. This is then used to derive the velocity autocorrelation function (VACF) and mean-squared displacement (MSD) of a particle undergoing nondiffusive Brownian motion.

In Sec. II, an integral expression for the time-dependent velocity of a perfectly slipping sphere is derived. In Sec. III, we calculate the VACF and MSD for a perfectly slipping sphere and compare to a no-slip sphere. In Sec. IV, we calculate the thermal force power spectral density (FPSD) of a particle with arbitrary slip length. A conclusion is offered in Sec. V.

II. CALCULATION OF THE TIME-DEPENDENT VELOCITY

Consider a perfectly slipping sphere under a force $\boldsymbol{F}_A(t)$ that is applied at $t = 0$ (and zero beforehand). We thus proceed by taking the Laplace transform of (3), which yields

$$\frac{4}{3}\pi a^3 \rho_b s\tilde{\boldsymbol{U}}(s) = -4\pi\mu a\tilde{\boldsymbol{U}}(s) - \frac{2}{3}\pi\rho a^3 s\tilde{\boldsymbol{U}}(s) - s\tilde{G}(s)\tilde{\boldsymbol{U}}(s) + \tilde{\boldsymbol{F}}_A(s), \tag{5}$$

where s is the Laplace transform variable and the tilde decoration denotes a Laplace transformed quantity. The Laplace transform of the memory kernel is

$$\tilde{G}(s) = 8\pi\mu a\left[\frac{9\nu}{a^2}\left(\frac{sa^2}{9\nu} + \sqrt{\frac{sa^2}{9\nu}}\right)\right]^{-1}. \tag{6}$$

Combining (5) and (6) gives

$$\tilde{\boldsymbol{U}}(\hat{s}) = \frac{1}{6\pi\mu a\gamma}\frac{\tilde{\boldsymbol{F}}_A(\hat{s})(1+\hat{s}^{1/2})}{\hat{s}^{3/2} + \hat{s} + 2\gamma^{-1}\hat{s}^{1/2} + \frac{2}{3}\gamma^{-1}}, \tag{7}$$

where $\hat{s} = sa^2/9\nu$ and $\gamma = 1 + 2\rho_b/\rho$. The three roots of the denominator of the second fraction in (7) are

$$\eta = -\tfrac{1}{3} - \alpha + \beta, \tag{8}$$

$$\zeta = -\tfrac{1}{3} + \tfrac{1}{2}(1 + i\sqrt{3})\alpha - \tfrac{1}{2}(1 - i\sqrt{3})\beta, \tag{9}$$

$$\zeta^* = -\tfrac{1}{3} + \tfrac{1}{2}(1 - i\sqrt{3})\alpha - \tfrac{1}{2}(1 + i\sqrt{3})\beta, \tag{10}$$

where η is real, ζ^* is the complex conjugate of ζ, $i = \sqrt{-1}$, and

$$\alpha = \frac{2^{1/3}[-1 + 6\gamma^{-1}]}{3[-2 + \sqrt{4 + 4(-1 + 6\gamma^{-1})^3}]^{1/3}}, \tag{11}$$

$$\beta = \frac{1}{3(2^{1/3})}[-2 + \sqrt{4 + 4(-1 + 6\gamma^{-1})^3}]^{1/3}. \tag{12}$$

We now factor the cubic in $\hat{s}^{1/2}$ in the denominator of the second fraction in (7) to obtain

$$\tilde{\boldsymbol{U}}(\hat{s}) = \frac{1}{6\pi\mu a\gamma}\left[\frac{\tilde{\boldsymbol{F}}_A(\hat{s})(1+\hat{s}^{1/2})}{(\hat{s}^{1/2} - \eta)(\hat{s}^{1/2} - \zeta)(\hat{s}^{1/2} - \zeta^*)}\right]. \tag{13}$$

Next, (13) is separated into two fractions

$$\tilde{\boldsymbol{U}}(\hat{s}) = \frac{1}{6\pi\mu a\gamma}\left[\frac{\tilde{\boldsymbol{F}}_A(\hat{s})}{(\hat{s}^{1/2} - \eta)(\hat{s}^{1/2} - \zeta)(\hat{s}^{1/2} - \zeta^*)} + \frac{\hat{s}\tilde{\boldsymbol{F}}_A(\hat{s}) + \boldsymbol{F}_A(0) - \boldsymbol{F}_A(0)}{\hat{s}^{1/2}(\hat{s}^{1/2} - \eta)(\hat{s}^{1/2} - \zeta)(\hat{s}^{1/2} - \zeta^*)}\right], \tag{14}$$

where the numerator of the second fraction in (14) has $\boldsymbol{F}_A(0)$ added and subtracted for simplification purposes later. We write (14) in shorthand as

$$\tilde{\boldsymbol{U}}(\hat{s}) = \frac{1}{6\pi\mu a\gamma}[\tilde{\boldsymbol{F}}_A(\hat{s})\tilde{M}_1(\hat{s}) + [\hat{s}\tilde{\boldsymbol{F}}_A(\hat{s}) - \boldsymbol{F}_A(0)]\tilde{M}_2(\hat{s}) + \boldsymbol{F}_A(0)\tilde{M}_2(\hat{s})], \tag{15}$$

where

$$\tilde{M}_1(\hat{s}) = [(\hat{s}^{1/2} - \eta)(\hat{s}^{1/2} - \zeta)(\hat{s}^{1/2} - \zeta^*)]^{-1}, \tag{16}$$

and

$$\tilde{M}_2(\hat{s}) = [\hat{s}^{1/2}(\hat{s}^{1/2} - \eta)(\hat{s}^{1/2} - \zeta)(\hat{s}^{1/2} - \zeta^*)]^{-1}. \tag{17}$$

We invert back to the time domain using the Laplace transform identities [10]

$$\mathcal{L}^{-1}\left[\frac{1}{\hat{s}^{1/2}(\hat{s}^{1/2} + b)}\right] = e^{b^2\hat{t}}\,\mathrm{erfc}(b\sqrt{\hat{t}}) \tag{18}$$

and

$$\mathcal{L}^{-1}\left[\frac{1}{\hat{s}^{1/2} + b}\right] = \frac{1}{(\pi\hat{t})^{1/2}} - be^{b^2\hat{t}}\,\mathrm{erfc}(b\sqrt{\hat{t}}), \tag{19}$$

where $\mathcal{L}^{-1}$ denotes the inverse Laplace transform and $\hat{t} = 9t\nu/a^2$. Hence, the time-dependent velocity is

$$\boldsymbol{U}(\hat{t}) = \frac{3}{2\pi\rho a^3\gamma}\left[\int_0^{\hat{t}}\boldsymbol{F}_A(\tau)M_1(\hat{t} - \tau)d\tau + \int_0^{\hat{t}}\frac{d\boldsymbol{F}_A(\tau)}{d\tau}M_2(\hat{t} - \tau)d\tau + \boldsymbol{F}_A(0)M_2(\hat{t})\right] \tag{20}$$

in which

$$M_1(\hat{t}) = \frac{1}{(\eta-\zeta)(\eta-\zeta^*)}\left[\frac{1}{(\pi\hat{t})^{1/2}} + \eta e^{\eta^2\hat{t}}\,\mathrm{erfc}(-\eta\sqrt{\hat{t}})\right] - \frac{1}{(\eta-\zeta)(\zeta-\zeta^*)}\left[\frac{1}{(\pi\hat{t})^{1/2}} + \zeta e^{\zeta^2\hat{t}}\,\mathrm{erfc}(-\zeta\sqrt{\hat{t}})\right] + \frac{1}{(\eta-\zeta^*)(\zeta-\zeta^*)}\left[\frac{1}{(\pi\hat{t})^{1/2}} + \zeta^* e^{\zeta^{*2}\hat{t}}\,\mathrm{erfc}(-\zeta^*\sqrt{\hat{t}})\right], \tag{21}$$

and

$$M_2(\hat{t}) = \frac{1}{(\eta-\zeta)(\eta-\zeta^*)}\left[\eta e^{\eta^2\hat{t}}\,\mathrm{erfc}(-\eta\sqrt{\hat{t}})\right] - \frac{1}{(\eta-\zeta)(\zeta-\zeta^*)}\left[\zeta e^{\zeta^2\hat{t}}\,\mathrm{erfc}(-\zeta\sqrt{\hat{t}})\right] + \frac{1}{(\eta-\zeta^*)(\zeta-\zeta^*)}\left[\zeta^* e^{\zeta^{*2}\hat{t}}\,\mathrm{erfc}(-\zeta^*\sqrt{\hat{t}})\right], \tag{22}$$

and τ is a dimensionless integration variable. Using integration by parts and the fact that $M_2(0) = 0$, (20) simplifies to

$$\boldsymbol{U}(\hat{t}) = \frac{3}{2\pi\rho a^3\gamma}\left[\int_0^{\hat{t}} \boldsymbol{F}_A(\tau)\left(M_1(\hat{t}-\tau) - \frac{dM_2(\hat{t}-\tau)}{d\tau}\right)d\tau\right], \tag{23}$$

where

$$M_1(\hat{t}) - \frac{dM_2(\hat{t})}{d\tau} = \frac{\eta(\eta+1)}{(\eta-\zeta)(\eta-\zeta^*)}e^{\eta^2\hat{t}}\,\mathrm{erfc}(-\eta\sqrt{\hat{t}}) - \frac{\zeta(\zeta+1)}{(\eta-\zeta)(\zeta-\zeta^*)}e^{\zeta^2\hat{t}}\,\mathrm{erfc}(-\zeta\sqrt{\hat{t}}) + \frac{\zeta^*(\zeta^*+1)}{(\eta-\zeta^*)(\zeta-\zeta^*)}e^{\zeta^{*2}\hat{t}}\,\mathrm{erfc}(-\zeta^*\sqrt{\hat{t}}). \tag{24}$$

Equation (23) gives the time-dependent velocity of a perfectly slipping sphere as an integral of the history of the force it has been subject to; the memory of that force is weighted by the kernel (24). Unfortunately, the complexity of the kernel means that (23) must, in general, be evaluated by a numerical quadrature. An integral expression for the velocity of a no-slip sphere analogous to (23) can be obtained from solution of (1) [11], which also requires numerical evaluation in general. In the next section we show that an analytical evaluation is possible for an impulsive force, which is relevant to Brownian motion and thus of particular practical value.

III. MOTION UNDER AN IMPULSIVE FORCE AND APPLICATION TO NONDIFFUSIVE BROWNIAN MOTION

Hinch [12] demonstrated that the solution of the BBO equation under an impulsive force of magnitude kT, where k is Boltzmann's constant, and T is the absolute temperature, yields the time-dependent velocity autocorrelation function (VACF) of a rigid, no-slip sphere. Let us denote the VACF as $\boldsymbol{R} = R(t)\boldsymbol{I}$, where $\boldsymbol{I}$ is the identity tensor: Then the solution of (1) under a force impulse $\boldsymbol{F}_A(t) = \boldsymbol{M}\delta(t)$, where $\boldsymbol{M}$ is a constant vector of magnitude kT and $\delta(t)$ is the Dirac delta function, gives [12]

$$R(t) = \frac{kT}{2\pi a^3\rho\left(5-8\frac{\rho_b}{\rho}\right)^{1/2}}\left(\frac{a^2}{\nu}\right)^{1/2} \times \left[\alpha_+ e^{\alpha_+^2 t}\,\mathrm{erfc}(\alpha_+\sqrt{t}) - \alpha_- e^{\alpha_-^2 t}\,\mathrm{erfc}(\alpha_-\sqrt{t})\right], \tag{25}$$

where

$$\alpha_\pm = \frac{1}{\gamma}\left(\frac{\nu}{a^2}\right)^{1/2}\frac{3}{2}\left[3 \pm \left(5 - 8\frac{\rho_b}{\rho}\right)^{1/2}\right]. \tag{26}$$

Here, at long times, $t\nu/a^2 \to \infty$, the VACF algebraically decays as $t^{-3/2}$. Alder and Wainwright saw this decay, or "long-time tail," using molecular dynamics simulations [13] as well as numerical solutions to the Navier-Stokes equations [14]. Comparatively, an incorrect exponential decay is predicted when neglecting unsteady forces, i.e., retaining only the quasisteady drag in (1). Weitz *et al.* [15] used diffusing-wave spectroscopy to experimentally observe this long-time algebraic decay for an ensemble of particles. Their experimental results for the time-dependent diffusivity show good agreement with the theoretical result obtained from (25). Paul and Pusey observed the long-time tail in Brownian motion using photon correlation dynamic laser light scattering [16]. More recently, Kheifets *et al.* [17] and Franosch *et al.* [18] have observed the long-time tail at the single-particle level using optical tweezers.

From (23), the VACF of a perfectly slipping sphere under a force impulse of magnitude kT is

$$R(\hat{t}) = \frac{3kT}{2\pi\rho a^3\gamma}\left[\frac{\eta(\eta+1)}{(\eta-\zeta)(\eta-\zeta^*)}e^{\eta^2\hat{t}}\,\mathrm{erfc}(-\eta\sqrt{\hat{t}}) - \frac{\zeta(\zeta+1)}{(\eta-\zeta)(\zeta-\zeta^*)}e^{\zeta^2\hat{t}}\,\mathrm{erfc}(-\zeta\sqrt{\hat{t}}) + \frac{\zeta^*(\zeta^*+1)}{(\eta-\zeta^*)(\zeta-\zeta^*)}e^{\zeta^{*2}\hat{t}}\,\mathrm{erfc}(-\zeta^*\sqrt{\hat{t}})\right], \tag{27}$$

which is plotted in Fig. 1. The long-time behavior of the VACF is calculated using the asymptotic approximation for the complex complementary error function

$$\lim_{z\to\infty}\mathrm{erfc}(z) \sim \frac{e^{-z^2}}{z\pi^{1/2}}\sum_{n=0}^{\infty}(-1)^n\frac{(2n)!}{n!(4z^2)^n} \quad \text{for } |\arg(z)| < 3\pi/4, \tag{28}$$

where z is a complex variable. Using the first three terms in this series and substituting (28) into (27) yields

$$\lim_{\hat{t}\to\infty} R(t) = \frac{kT}{12\pi^{3/2}\rho a^3}\left[\left(\frac{a^2}{\nu t}\right)^{3/2} + \left(\frac{a^2}{\nu t}\right)^{5/2}\left(\frac{\rho_b}{\rho} - 1\right) + O\left[\left(\frac{a^2}{\nu t}\right)^3\right]\right], \tag{29}$$

the leading-order term is identical to the no-slip sphere case. Physically, at long times momentum diffuses far enough away that the boundary condition on the sphere is unimportant: Both

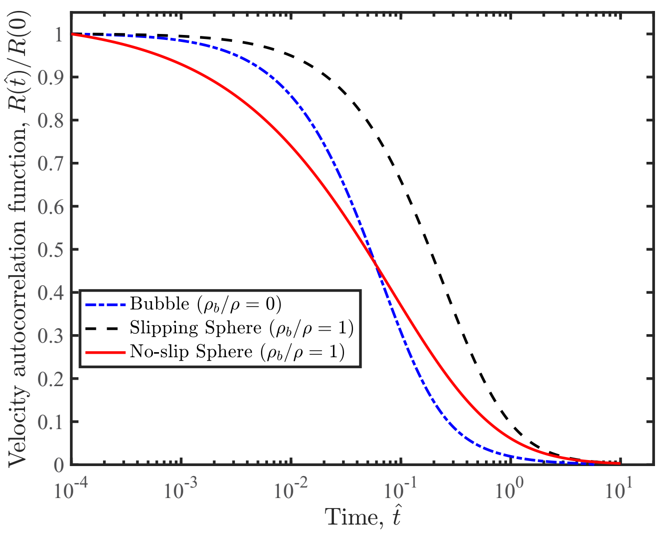

FIG. 1. VACF of a rigid, neutrally buoyant no-slip and perfectly slipping sphere, and an inviscid bubble vs dimensionless time $\hat{t}$, where $\hat{t} = t\nu/a^2$.

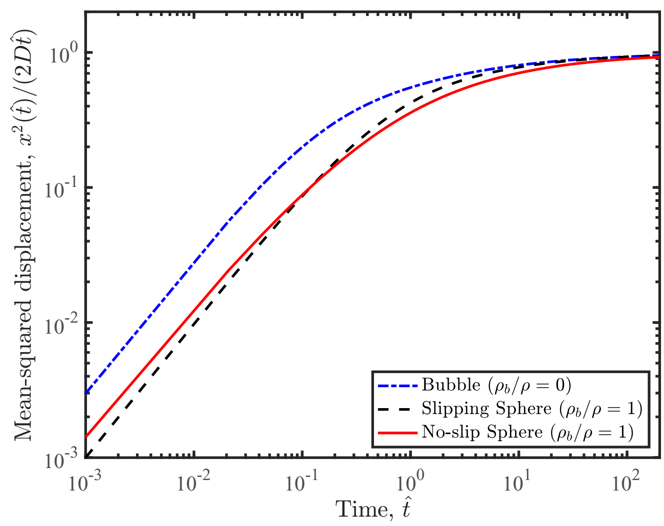

FIG. 2. MSD of a neutrally buoyant no-slip sphere, neutrally buoyant slipping sphere, and an inviscid bubble, where $\hat{t} = t\nu/a^2$ and D is the steady diffusivity.

a no-slip rigid sphere and perfectly slipping sphere appear as an impulsive Stokeslet leading to an identical leading-order decay of $R(t)$. The second term in (29) differs from that of a no-slip sphere: Instead of $(\rho_b/\rho - 1)$, the long-time asymptotic expansion of (25) has a coefficient of $(4\rho_b/\rho - 7)/6$. Note, the leading-order decay of the angular VACF (scaling as $t^{-5/2}$) is sensitive to particle geometry [19]. Thus, it may be that the angular VACF of a perfectly (or even partially) slipping sphere is different at leading order to a no-slip sphere.

The short-time limit of the VACF is calculated using the expansion

$$e^{z^2}\,\mathrm{erfc}(-z) \sim 1 + \frac{2z}{\pi^{1/2}} + z^2 + \frac{4z^3}{3\pi^{1/2}} + \cdots \text{ as } z \to 0. \tag{30}$$

Substituting the above into (27) yields

$$R(\hat{t}) \sim \frac{3kT}{2\pi\rho a^3\gamma}\left[1 - \frac{2}{\gamma}\hat{t} + \frac{16}{9\pi^{1/2}}\frac{1}{\gamma}\hat{t}^{3/2} + \cdots\right] \text{ as } \hat{t} \to 0. \tag{31}$$

Note, the VACF of a no-slip sphere has a $\hat{t}^{1/2}$ contribution at short times; evidently, the perfectly slipping sphere does not. Physically, this occurs because the no-slip boundary conditions results in a more efficient transfer of momentum from the particle to the fluid; thus the VACF decays more rapidly at short times for a rigid sphere.

When $\hat{t} = 0$, the VACF is

$$R(0) = \frac{kT}{\frac{4}{3}\pi a^3\left(\rho_b + \frac{1}{2}\rho\right)}, \tag{32}$$

which is kT divided by the sum of the particle mass and the added mass. However, the equipartition theorem states that properly $R(0) = kT/(\frac{4}{3}\pi a^3\rho_b)$. The discrepancy lies in our assumption that the fluid is incompressible. Relaxing the assumption recovers the correct $R(0)$ as shown by Zwanzig and Bixon [20]. Specifically, compressible effects result in a drop of $R(0)$ from its proper initial value to that in (32) over a duration that is comparable to the timescale required for a sound wave to travel across the particle, i.e., a/c, where c is the speed of sound. Importantly, this timescale is typically much shorter than the momentum diffusion time, a^2/ν. Thus, it is a reasonable approximation to assume the fluid is incompressible when calculating the unsteady momentum diffusion from the impulsively forced particle.

Let the mean-squared displacement (MSD) of the particle be $x^2(t)\boldsymbol{I}$. The MSD is defined in terms of the VACF by [15]

$$x^2(\hat{t}) = 2\int_0^{\hat{t}} (\hat{t} - \tau)R(\tau)\,d\tau. \tag{33}$$

Substituting (27) into (33) yields

$$\begin{aligned}\frac{x^2(\hat{t})}{2D\hat{t}} = \frac{2}{3}\Bigg[&\frac{9}{4\hat{t}}\left(3 - 2\frac{\rho_b}{\rho}\right) + \frac{3}{2} - \frac{6}{\sqrt{\pi\hat{t}}}\\ &+ \frac{1}{\hat{t}\gamma}\Bigg\{\frac{(\eta+1)}{\eta^3(\eta-\zeta)(\eta-\zeta^*)}e^{\eta^2\hat{t}}\,\mathrm{erfc}(-\eta\sqrt{\hat{t}})\\ &- \frac{(\zeta+1)}{\zeta^3(\eta-\zeta)(\zeta-\zeta^*)}e^{\zeta^2\hat{t}}\,\mathrm{erfc}(-\zeta\sqrt{\hat{t}})\\ &+ \frac{(\zeta^*+1)}{\zeta^{*3}(\eta-\zeta^*)(\zeta-\zeta^*)}e^{\zeta^{*2}\hat{t}}\,\mathrm{erfc}(-\zeta^*\sqrt{\hat{t}})\Bigg\}\Bigg],\end{aligned} \tag{34}$$

and the MSD is plotted in Fig. 2. Here, $D = kT/4\pi\mu a$, which is the long-time diffusion coefficient of a perfectly slipping sphere first calculated by Sutherland [21]. In that paper, Sutherland also gave a formula for D at an arbitrary value of the ratio of the slip length to particle radius. As this ratio becomes small one recovers the familiar result $D = kT/6\pi\mu a$ usually attributed to Einstein in his celebrated 1905 paper on Brownian motion [22]. In fact, Sutherland himself derived this result one year earlier in 1904 [23] (albeit with an unfortunate typographical error where k was replaced by the universal gas constant). This has prompted some to rename the formula $D = kT/6\pi\mu a$ as the "Stokes-Einstein-Sutherland" [24] or "Sutherland-Einstein" diffusivity [25].

At long times, the MSD is from (34)

$$\frac{x^2(\hat{t})}{2D\hat{t}} \sim 1 - \frac{4}{\sqrt{\pi \hat{t}}} + \frac{3}{2\hat{t}}\left(3 - 2\frac{\rho_b}{\rho}\right) + \cdots, \quad (35)$$

with an algebraic error due to the long-time tail of the VACF.

The short-time limit of the MSD is from (34)

$$\frac{x^2(\hat{t})}{2D\hat{t}} \sim \frac{1}{3\gamma}\hat{t} - \frac{2}{9\gamma^2}\hat{t}^2 + \cdots, \quad (36)$$

corresponding to ballistic motion at leading order.

IV. THERMAL FORCE POWER SPECTRAL DENSITY OF A PARTIALLY SLIPPING SPHERE

We now consider a rigid sphere over which fluid partially slips. Let λ be the slip length. The equivalent to the BBO equation for a partially slipping sphere is [26–28]

$$\frac{4}{3}\pi a^3 \rho_b \frac{d\boldsymbol{U}(t)}{dt} = -6\pi\mu a W(\lambda)\boldsymbol{U}(t) - \frac{2}{3}\pi\rho a^3 \frac{d\boldsymbol{U}(t)}{dt} - \int_{-\infty}^{t} J(t-t')\frac{d\boldsymbol{U}(t)}{dt}dt' + \boldsymbol{F}_A(t), \quad (37)$$

where the new memory kernel

$$J(t) = H(\lambda)6\pi\mu a\left(e^{(H/W^2)^2 t\nu/a^2}\right)\mathrm{erfc}\left((H/W^2)\sqrt{\frac{t\nu}{a^2}}\right). \quad (38)$$

We have also defined

$$W(\lambda) = \frac{1+2\lambda/a}{1+3\lambda/a}, \text{ and } H(\lambda) = \frac{(1+2\lambda/a)^2}{\lambda/a(1+3\lambda/a)}. \quad (39)$$

Following the same procedure as Sec. II, the frequency-dependent velocity in the Laplace space is

$$\tilde{\boldsymbol{U}}(\hat{s}) = \frac{3\tilde{\boldsymbol{F}}_A(\hat{s})}{2\pi\mu a\gamma(W^2/H)}\left[\frac{1+(W^2/H)\hat{s}^{1/2}}{\hat{s}^{3/2} + (H/W^2)\hat{s} + 9(H+W)\gamma^{-1}\hat{s}^{1/2} + 9(H/W)\gamma^{-1}}\right]. \quad (40)$$

The presence of the coefficients in (40) involving W and H mean that an inversion of (40), while technically possible, results in an expression that is far too lengthy to be of value. Instead, we use (40) to analytically determine the thermal force power spectral density (FPSD) of a partially slipping sphere in Brownian motion. Mo *et al.* [29] recently numerically computed this FPSD and suggested it to be a suitable quantity from which to infer slip length from measurement of single-particle Brownian motion in an optical trap. The FPSD is defined as [29]

$$S_F(\hat{\omega}) = 4\pi kT\mathcal{R}\left(\frac{|\tilde{\boldsymbol{F}}_A(\hat{\omega})|}{|\tilde{\boldsymbol{U}}(\hat{\omega})|}\right), \quad (41)$$

where $\mathcal{R}$ denotes the real part and the term in the parentheses is the Fourier transform of the time-dependent hydrodynamic resistance. Here, $\hat{\omega} = \omega\nu/a^2$ is a normalized Fourier-space frequency. The Fourier-space resistance is readily determined from (40) via the analytic continuation $\hat{s} \to i\hat{\omega}$. Solving for $\mathcal{R}(|\tilde{\boldsymbol{F}}_A(\hat{\omega})|/|\tilde{\boldsymbol{U}}(\hat{\omega})|)$ yields

$$\mathcal{R}\left(\frac{|\tilde{\boldsymbol{F}}_A(\hat{\omega})|}{|\tilde{\boldsymbol{U}}(\hat{\omega})|}\right) = \frac{2}{3}\pi\mu a(W^2/H)\left[\frac{9(W^2+W^3/H)\hat{\omega} + \frac{9\sqrt{2}}{2}(H+2W)\hat{\omega}^{1/2} + 9(H/W)}{(W^4/H^2)\hat{\omega} + \sqrt{2}(W^2/H)\hat{\omega}^{1/2} + 1}\right]. \quad (42)$$

The FPSD is then simply calculated by substituting (42) into (41). Figure 3 shows the FPSD of a particle with varying slip length. Notably, the FPSD is independent of the density ratio. At higher frequencies, S_F becomes more sensitive to the effect of slip length. Since high frequency corresponds to short time, momentum only diffuses short distances from the particle. The difference created by having a slip condition is therefore more dramatic.

The high-frequency limit of (41) is

$$S_F(\hat{\omega}) \sim 24\pi^2\mu akT\left(H + W - \frac{\sqrt{2}}{2}\frac{H^2}{W^2}\hat{\omega}^{-1/2} + \cdots\right), \quad (43)$$

and is plotted in the solid blue line in Fig. 3. The high-frequency limit from (43) gives the approach to a constant FPSD as $\hat{\omega} \to \infty$ for any sphere with slip, however, the FPSD of a no-slip sphere will diverge as $\hat{\omega}^{1/2}$ as $\omega \to \infty$.

The low-frequency limit of (41) is

$$S_F(\hat{\omega}) \sim 24\pi^2\mu akT\left(W + \frac{\sqrt{2}}{2}H\hat{\omega}^{1/2} + \cdots\right), \quad (44)$$

and is plotted in the dashed blue line in Fig. 3. We hope that the analytical approximations (43) and (44) may prove useful in determining slip length from experimental measurements of non-diffusive Brownian motion.

V. CONCLUSION

An integral expression (23) for the translational velocity of a perfectly slipping spherical particle under a time-dependent applied force in unsteady Stokes flow is derived. We compare this result to that of a rigid, no-slip sphere and an inviscid spherical bubble. Under an impulsive force of magnitude kT, we calculate the VACF and MSD of a perfectly slipping particle undergoing non-diffusive Brownian motion. At long

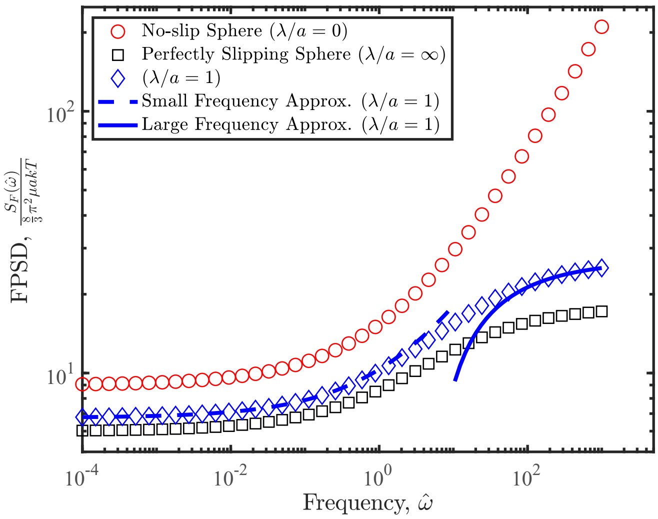

FIG. 3. FPSD of a particle normalized by $\frac{8}{3}\pi^2\mu akT$ vs dimensionless frequency, $\hat{\omega} = \omega a^2/\nu$. Asymptotic approximations are shown at small and large frequency for $\lambda/a = 1$.

times, we recover leading order algebraic $t^{-3/2}$ decay of the VACF of a perfectly slipping sphere which is identical to that of a no-slip sphere. That is, at long times, momentum diffuses far enough away from the sphere that the surface boundary condition is unimportant. The FPSD of a rigid sphere with arbitrary slip length is calculated. Short- and long-time asymptotic approximations are calculated, which we hope may be useful for inference of slip length from experimental measurements of non-diffusive Brownian motion.

Here, we assumed that an inviscid bubble is equivalent to a perfectly slipping sphere of constant radius and zero density. That is, we neglect the possibility that the radius of the bubble changes in time. Magnaudet and Legendre [30] have, in fact, computed the time-dependent hydrodynamic force on a bubble of varying radius in unsteady Stokes flow. They show that the history of the variation in bubble radius contributes to the unsteady viscous force on it [see Eq. (22b) in their paper]. Hence, one could use their expression for the time-dependent force in (3) to consider the motion of a bubble with time varying radius. However, the complexity of the unsteady viscous force would necessitate a numerical solution, i.e., an integral expression for the velocity akin to (23) would not be obtainable, we believe. Similarly, our analysis has neglected hydrodynamic interactions between particles and is thus only applicable to the unsteady motion of a single sphere. The consideration of particle-particle interactions would necessitate a major extension, as opposed to modification, of our analysis. That is, even at the pair (two-body) level one would have to solve the unsteady Stokes equations around two oscillating spheres to determine the influence of hydrodynamic interactions on the frequency-dependent drag felt by each particle, which is certainly a challenging task. Finally, Daitche and Tél [1] demonstrated that the history force on a no-slip sphere is relevant in the correct prediction of particle trajectories and chaotic advection in an ambient flow. An interesting problem for future work would be to quantify how the different form of the history force for a perfectly slipping sphere affects such dynamics in ambient flows.

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[1] A. Daitche and T. Tél, Memory Effects are Relevant for Chaotic Advection of Inertial Particles, Phys. Rev. Lett. **107**, 244501 (2011).

[2] S. Olivieri, F. Picano, G. Sardina, D. Ludicone, and L. Brandt, The effect of the Basset history force on particle clustering in homogeneous and isotropic turbulence, Phys. Fluids **26**, 041704 (2014).

[3] A. J. T. M. Mathijssen, J. Culver, M. S. Bhamla, and M. Prakash, Collective intercellular communication through ultra-fast hydrodynamic trigger waves, Nature (London) **571**, 560 (2019).

[4] C. L. Wirth, P. J. Sides, and D. C. Prieve, Electrolyte dependence of particle motion near an electrode during ac polarization, Phys. Rev. E **87**, 032302 (2013).

[5] S. L. Seyler and S. Pressé, Long-time persistence of hydrodynamic memory boosts microparticle transport, Phys. Rev. Res. **1**, 032003 (2019).

[6] M. Maxey and J. Riley, Equation of motion for a small rigid sphere in a nonuniform flow, Phys. Fluids **26**, 883 (1983).

[7] S.-M. Yang and L. G. Leal, A note on memory-integral contributions to the force on an accelerating spherical drop at low Reynolds number, Phys. Fluids A **3**, 1822 (1991).

[8] F. A. Morrison and M. B. Stewart, Small bubble motion in an accelerating fluid, J. Appl. Mech. **97**, 399 (1976).

[9] E. E. Michaelides and Z.-G. Feng, The equation of motion of a small viscous sphere in and unsteady flow with interface slip, Int. J. Multiphase Flow **21**, 315 (1995).

[10] F. Oberhettinger and L. Badii, *Tables of Laplace Transforms* (Springer, Berlin, 1973).

[11] S. Kim and S. J. Karrila, *Microhydrodynamics Principles and Selected Applications* (Dover, New York, 1991).

[12] E. J. Hinch, Application of the Langevin equation in fluid suspensions, J. Fluid Mech. **72**, 499 (1975).

[13] B. J. Alder and T. E. Wainwright, Velocity Autocorrelations for Hard Spheres, Phys. Rev. Lett. **18**, 988 (1967).

[14] B. J. Alder and T. E. Wainwright, Decay of the velocity autocorrelation function, Phys. Rev. A **1**, 18 (1970).

[15] D. A. Weitz, D. J. Pine, P. N. Pusey, and R. J. A. Tough, Nondiffusive Brownian Motion Studied by Diffusing-Wave Spectroscopy, Phys. Rev. Lett. **63**, 1747 (1989).

[16] G. L. Paul and P. N. Pusey, Observation of a long-time tail in Brownian motion, J. Phys. A: Math. Gen. **14**, 3301 (1981).

[17] S. Kheifets, A. Simha, K. Melin, T. Li, and M. G. Raizen, Observation of Brownian motion in liquids at short times:

Instantaneous velocity and memory loss, Science **343**, 1493 (2014).

[18] T. Franosch, M. Grimm, M. Belushkin, F. M. Mor, G. Foffi, L. Forró, and S. Jeney, Resonances arising from hydrodynamic memory in Brownian motion, Nature (London) **478**, 85 (2011).

[19] R. Hocquart and E. J. Hinch, The long-time tail of the angular-velocity autocorrelation function for a rigid Brownian particle of arbitrary centrally symmetric shape, J. Fluid Mech. **137**, 217 (1983).

[20] R. Zwanzig and M. Bixon, Compressiblity effects in the hydrodynamic theory of Brownian motion, J. Fluid Mech. **69**, 21 (1975).

[21] W. Sutherland, A dynamical theory of diffusion for nonelectrolytes and the molecular mass of albumin, London, Edinburgh Dublin Philos. Mag. J. Sci. **9**, 781 (1905).

[22] A. Einstein, Investigations on the theory of the Brownian movement, Ann. Phys. **17**, 549 (1905).

[23] W. Sutherland, The measurement of large molecular masses, in *Report of the Tenth Meeting of the Australasian Association for the Advancement of Science*, edited by G. M. Thomson (The Australasian Association for the Advancement of Science, Dunedin, 1904), pp. 117–121.

[24] A. S. Khair and J. F. Brady, "Microviscoelasticity" of colloidal dispersions, J. Rheol. **49**, 1449 (2005).

[25] T. Damour, O. Darrigol, and V. Rivasseau, *Einstein, 1905-2005: Poincaré Seminar 2005* (Springer, Berlin, 2006).

[26] D. Legendre, A. Rachih, C. Souilliez, S. Charton, and E. Climent, Basset-Boussinesq history force of a fluid sphere, Phys. Rev. Fluids **4**, 073603 (2019).

[27] R. Gatignol, The Faxen formulas for a rigid particle in an unsteady non-uniform stokes flow, J. Mec. Theor. Appl. **2**, 143 (1983).

[28] A. Premlata and H.-H. Wei, The Basset problem with dynamic slip: Slip-induced memory effect and slip-stick transition, J. Fluid Mech. **866**, 431 (2019).

[29] J. Mo, A. Simha, and M. G. Raizen, Brownian motion as a new probe for wettability, J. Chem. Phys. **146**, 134707 (2017).

[30] J. Magnaudet and D. Legendre, The viscous drag force on a spherical bubble with a time-dependent radius, Phys. Fluids **10**, 550 (1998).