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Comment on ''Long-time behavior of the angular velocity autocorrelation function'' [J. Chem. Phys. 105, 9695 (1996)]

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It has been known since the work of Stokes in 1851 that in the calculation of the linear frequency-dependent friction coefficients of a body immersed in a viscous fluid the stick boundary condition must be applied at the undisplaced body surface. It is true that the actual boundary condition holds at the displaced surface, but, since displacement is the time integral of velocity, it contributes nonlinearly to the response to applied force and torque.

The calculation of the linear frequency-dependent friction matrix, based on Stokes' method, shows that the coefficient of the long-time tail in the translational velocity of the body after a sudden small impulse is independent of shape and size of the body.[1] On the other hand, the coefficient of the long-time tail in the rotational velocity after a sudden small applied torque depends on the shape of the body, both in two and three dimensions.[2,3] On account of the fluctuation–dissipation theorem the same results hold for the long-time tail of the translational and rotational velocity autocorrelation function of Brownian motion.

Masters[4] questions our result[2,3] for the rotational velocity, and claims that somehow it holds only for a body that is kept fixed. According to his calculation the coefficient of the long-time tail of the rotational velocity is independent of the shape of the body. His argument hinges on the application of the stick boundary condition at the displaced body surface. Hence he deals with a nonlinear effect. In the discussion of the effect his reasoning is far from rigorous. Following his Eq. (7) he assumes that at long times the reorientation of the particle is governed by the rotational diffusion equation. This introduces a stochastic effect in a calculation that should be purely hydrodynamic. In hydrodynamics the reorientation of the body is given by the time-integral of the angular velocity, and the variation of the latter is fully deterministic.

In our previous Comment[5] we have been careful to distinguish between the angular velocity relaxation function $\psi(t)$ and the correlation function $C_R(t)$ of Brownian motion. According to the fluctuation–dissipation theorem the correlation function is proportional to the relaxation function in the linear regime. The relaxation function has been determined for a lattice Boltzmann fluid in computer simulation.[6] For small initial angular velocity the long-time tail of the relaxation function agrees well with our calculations from linear hydrodynamics.[2,3] For large initial angular velocity the behavior on the same time scale is quite different, as evident from the figures in Ref. 6. This clearly shows the presence of nonlinear effects. For large initial angular velocity the coefficient of the long-time tail of the velocity relaxation function becomes independent of shape, in agreement with the prediction of Masters and Keyes.[7] In our opinion, in the light of the above remarks on Ref. 4, a revision of the theory of the nonlinear effect would be desirable.

Finally, we note that the computer simulation[6] and the calculation by Masters[4] are for a lattice Boltzmann fluid for which the linearized hydrodynamic equations apply. The nonlinear effects for this system are due only to the kinematics of rigid body motion. In real fluids the hydrodynamic equations are nonlinear, and this will have an additional effect.

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