Summary. The Fokker-Planck equation is derived for an arbitrary-shaped, molecularly structured Brownian particle near a molecularly structured surface. The derivation leads to explicit expressions for the grand friction tensor in terms of time correlation operators. Rotational and translational friction tensors for some illustrative cases are obtained from these expressions using molecular dynamics methods. A combined molecular/Brownian dynamics method is also presented, enabling the determination of long-time dynamics of molecularly structured macromolecules in molecular fluids. This study has notable significance in applications in biological physics involving site specific adsorption of macromolecules onto cells and other surfaces.

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Introduction. Using the method of multiple time scales¹ the Fokker-Planck (FP) equation can be derived for an arbitrary, molecularly constructed Brownian particle near a molecularly constructed wall (adsorbate). The derivation exploits the disparate time scales for the dynamics of a Brownian particle and leads to a fluctuation-dissipation relation for the grand particle friction tensor². In these types of relationships, also called Green-Kubo relations, the dynamic property is determined from an equilibrium time correlation function. Physically, one is studying the natural fluctuations about a given equilibrium state in energy, stress, etc. Although such fluctuations take place over very small time scales, on the order of picoseconds, it is possible to study these effects with molecular dynamics (MD) computational methods. The rate of decay of the time correlation functions that describes the fluctuations about equilibrium states can be related to the dynamic (transport) property via the Green-Kubo relations. Although the method is some forty years old, advances in high speed computing have revitalized it.

¹ Cukier and Deutch, Phys Rev., 177, 240-244 (1969)
² The molecular theory of Brownian motion is often referred to as LLRD theory after Lebowitz, Rubin, Resibois and Davis [Phys Rev., 131, 2381 (1969); Physica, 30, 1077 (1964)], but it should be renamed to KLLRD theory after the pioneering work of John Gamble Kirkwood. Kirkwood presented the original molecular theory of Brownian motion in 1945 (J. Chem. Phys. – also, see “The Collected Works of John Gamble Kirkwood”) which encompassed the fluctuation-dissipation relation - Kirkwood’s work even preceded that of Green and Kubo.
Results and Discussions. In the presence of a wall, new terms appear in the derivation of the FP equation as a result of fluid molecular mediated interactions between the particle and the wall (molecular counterpart of “hydrodynamic interactions”)\(^3\). Molecular dynamics results are presented for some simplified cases of a molecularly constructed “spherical” particle near a molecular constructed “planar” wall\(^4\). This enables comparisons to known analytical studies from low Reynolds number hydrodynamics. It is shown that MD calculations of the force autocorrelation function lead to results in agreement with continuum hydrodynamics, except under conditions of particle-wall separation distances of a few molecules. Extensions to more practical, complex biological systems, where continuum methods break down, are also discussed.