Direct Observation of Rotational Brownian Motion of Spheres by NMR

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We present a new NMR method for the investigation of rotational Brownian motion based on the appearance of dipolar relaxation as the particles rotate. Our experimental results obtained on submicrometer polystyrene spheres in water confirm quantitatively the basic laws of rotational Brownian motion. The effects of hydrodynamic interactions and long-time tails are discussed.

Brownian motion, discovered by R. Brown in 1828, refers to the random movement of small objects like pollen particles dispersed in a fluid. The phenomenon affords an ideal way of studying the evolution of a system with a small number of degrees of freedom coupled to a heat bath, a central question in statistical mechanics. For example, it gave rise to the well-known Einstein relation which was a first form of the general fluctuation-dissipation theorem. More recently, Brownian motion has provided the first experimental evidence[1] for the so-called long-time tails, a very general phenomenon in dynamical systems. Despite its importance, Brownian motion has not been fully investigated however. In particular, not much experimental work has been done on rotational Brownian motion,[2] mainly by reason of the great difficulty in observing the rotation of small objects, especially spherical ones.

The aim of this Letter is to present an experimental study of the rotational Brownian motion of well defined objects—submicrometer polystyrene spheres in water—using a new NMR method which gives direct access to the diffusion coefficient D.

Analysis of the method.—This method is based on the nonadiabatic thermodynamic evolution of a nuclear-spin system (^{1}H belonging to the polystyrene spheres here) as its Hamiltonian changes with time. This change in our case results from the dependence of the secular dipolar Hamiltonian H_d on the orientation of the internuclear vectors with respect to the applied field. The lack of adiabaticity is detected by following the evolution of the system after a Jeener-Broekaert[3] sequence which creates a density matrix $\rho(0) = \underline{1} - \beta(0)H_d(0)$ corresponding to an equilibrium state with respect to $H_d(0)$. As the Hamiltonian evolves, ρ remains close to an adiabatic form $\rho = \underline{1} - \beta(t)H_d(t)$, but the inverse dipolar temperature $\beta(t)$ decreases with a relaxation rate which includes a contribution T_d^{-1} due to the motion.

Using the following formal solution for $\rho(t)$,

$$\rho(t) = \underline{1} - \beta(0)[\text{Tr}H_d^2(0)]^{1/2}\{\tilde{H}(t) - \int_0^t dt'\, U(t,t')\dot{\tilde{H}}(t')U^\dagger(t,t')\} \tag{1}$$

with

$$\tilde{H}(t) = H_d(t)/[\text{Tr}H_d^2(t)]^{1/2}, \quad U(t,t) = \underline{1}, \quad i\hbar\,(\partial/\partial t)U(t,t') = H_d(t)U(t,t'),$$

Jeener[4] has derived the following general expression for T_d^{-1} which is valid as long as the line shape retains its rigid form (i.e., for a rotational Brownian motion with $DT_2 \ll 1$, where T_2, 10^{-5} s in polystyrene, is the transverse relaxation time):

$$T_d^{-1} = \int_0^\infty dt\, \langle \text{Tr}\{\dot{\tilde{H}}(t)U(t,0)\dot{\tilde{H}}(0)U^\dagger(t,0)\}\rangle, \tag{2}$$

where the angular brackets denote a statistical average. We anticipate that the correlations between $\dot{\tilde{H}}(0)$ and $\dot{\tilde{H}}(t)$ die out fast enough that the departure in (2) of the spin evolution operator $U(t,0)$ from the identity operator can be fully neglected. Within this limit, it can be shown that one obtains for a rotating object

$$T_d^{-1} = 2\int_0^\infty dt\, \langle \vec{\Omega}(0)\cdot\vec{\Omega}(t)\rangle, \tag{3}$$

where $\Omega(t)$ is its angular velocity. By virtue of the Green-Kubo relation, one has then for a sphere subject to rotational Brownian motion[5,6]

$$T_d^{-1} = 6D. \qquad (4)$$

It is worth noting at this point that this is the same relation as is derived with use of elementary spin thermodynamics for the restricted class of rotational Brownian motion which arises from random, small, sudden, and widely separated $(\Delta t \gg T_2)$ angular jumps.

For an isolated sphere of radius a in a fluid of viscosity η, the theory[5,6] predicts a diffusion coefficient

$$D_0 = kT/8\pi\eta a^3. \qquad (5)$$

For a finite-volume fraction ϕ of such hard-core interacting spheres, we must take into account hydrodynamic interactions between spheres. They lead to a reduction of the diffusion coefficient:

$$D = D_0[1 - k_R\phi + O(\phi^2)], \qquad (6)$$

where the coefficient k_R has been recently determined[7] to be $k_R = \frac{5}{16}$. This value is notably smaller than the value predicted by effective medium theories[8] $k_R = \frac{5}{2}$, which is the same as that which one obtains by assuming that each particle moves in a uniform medium with the viscosity of the solution.

Our interpretation of the experimental data presented below is then based on the following formula deduced form (4), (5), and (6):

$$T_d = (4\pi\eta a^3/3kT)(1 + k_R\phi). \qquad (7)$$

Experimental results and discussion.—The samples consisted of lattices[9] of polystyrene spheres in H_2O or D_2O with monodispersities ranging from 2% to 10% on going from diameters of 1 to 0.09 μm. The average diameter was measured by transmission electron microscopy to within about 50 Å.

Although the particles show surface charge ($\sim 10^3 e$ when $2a \sim 0.1$ μm), the Coulomb interactions between spheres are strongly screened by the ions present in the solution as soon as they are separated by more than 10 Å, so that a hard-core interparticle potential is a good approximation.[9]

In order to get good enough NMR signal-to-noise ratios, the volume concentration used is $\phi \sim 0.08$. The experiments have been carried out on the ^{1}H spin system of polystyrene at 30 MHz, in a home-made crossed-coil pulse spectrometer. We used as often as possible samples prepared in D_2O in order to avoid the large NMR signal from H_2O. The sample volume is 0.75 cm^3 and its temperature is regu-

lated within $0.25°$ C.

A time τ after the Jeener-Broekaert sequence, we apply an observation pulse and record the subsequent signal which is proportional to $\beta(\tau)$. This dipolar signal is accumulated up to 1024 times in a fast multichannel analyzer.

First of all, the intrinsic relaxation of $\beta(\tau)$ (that is the one induced by internal motion in bulk polystyrene) was measured as a function of temperature for each sample after drying it, or after concentrating it enough to suppress the rotational Brownian motion. In the whole of the region 275 K $\leq T \leq 303$ K the intrinsic relaxation time T_d^{int} (~ 1100 μsec) is almost constant and does not depend strongly on the sample. Since the Zeeman relaxation time T_{1Z} proved to be much longer (~ 1 sec) than the time scale (hundreds of microseconds) involved in the dipolar relaxation, it could be neglected.

For each run the intrinsic relaxation was subtracted from the one measured in the latex. The resultant curve was assumed to represent the dipolar relaxation due exclusively to rotational Brownian motion. Within the experimental accuracy, this relaxation was found to be exponential. The rate of the intrinsic relaxation sets an upper limit ($2a < 0.3$ μm) to the sphere diameter for which the measurements of the corresponding relaxation time T_d can be made with reasonable accuracy.

As appears clearly from expression (7) for the diffusion coefficient, there are two important parameters in the description of rotational Brownian motion: the viscosity η of the fluid and the radius a of the spheres. We have studied the variations of T_d with both.

The dependence on a has been investigated by measuring T_d for particle diameters between 0.1 and 0.3 μm. The results are shown in Fig. 1, together with the expected law (7) for $T = 296.2$ K. The agreement between theory and experiment is quite satisfactory. The viscosity of the fluid was verified (with use of a capillary viscometer) to be within 1% that of pure water at the same temperature. We assume $\eta = 0.933$ cP at 296.2 K for H_2O. The values for the samples in D_2O[10] have been reduced to that in H_2O by assuming the dependence of T_d on the fluid predicted by (7) and confirmed below. Although the volume concentration in our samples is not high enough to allow a precise determination of k_R, our results strongly support the conclusion that k_R is indeed smaller than $\frac{5}{2}$, indicating that screening of hydrodynamic interactions is effective for rotational Brownian motion.[7] We must point out that T_d has also been measured for
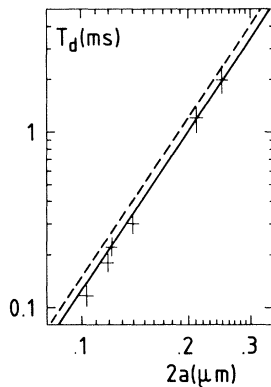
FIG. 1. Dependence of rotational Brownian motion on the size of the objects: The dipolar relaxation time T_d associated with rotational Brownian motion for polystyrene spheres in water at 296.2 K vs their diameter. The full line corresponds to the theoretical expression (7) where the coefficient k_R describing the effect of hydrodynamic interactions is set at the value $k_R = \frac{5}{16}$ according to hydrodynamic interactions (Ref. 7), and $\phi = 0.08$. The dashed line is the same but with $k_R = \frac{5}{2}$ as given by effective medium theory (Ref. 8).

larger spheres ($2a \sim 1$ μm) than those in Fig. 1. However, since the intrinsic relaxation mechanism is in this case much more efficient than rotational Brownian motion, only a lower bound value $T_d \gtrsim 20$ msec could be deduced. This result nevertheless confirms the strong slowing down of rotational Brownian motion as the particle diameter increases.

The effect of viscosity on D has been studied by varying the temperature in the range 275 K $\leq T \leq$ 300 K for three different samples in D_2O. As can be seen in Fig. 2, T_d varies as $\eta(T)/T$ as predicted by the relation (7). The Brownian particle diameters inferred from the best fits to our data with this relation are furthermore in good agreement with the electron microscopy measurements.

In view of this set of results we conclude that expression (7) accounts well for the dipolar relaxation induced by the rotational Brownian motion. We now assess the validity in our case of relation (3) upon which expression (7) relies and discuss the very intersting situation when the spin evolution due to the dipolar interactions, which has a characteristic time T_2, cannot be neglected during the decay of the angular velocity correlations.

We shall use for that purpose an approximation due to Jeener[4] which is simple enough to handle but keeps track of the evolution operators appearing in (2). It consists in replacing $U(t,0)\ddot{H}(0)U^\dagger(t,0)$ in (2) by $\exp(-t/T_2)\ddot{H}(0)$, and corresponds to as-
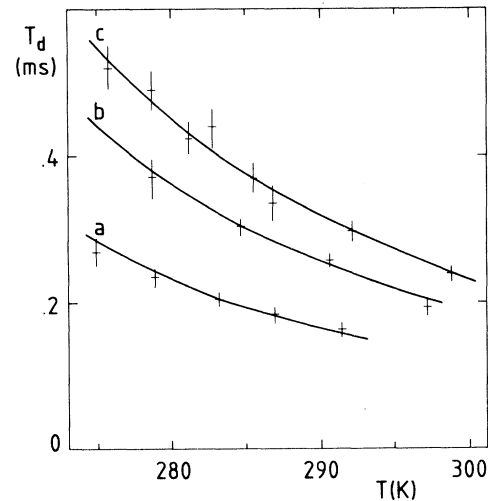

FIG. 2. Dependence of rotational Brownian motion on the viscosity of the fluid: Dipolar relaxation time T_d vs temperature for three samples in D_2O. The solid curves are proportional to $\eta(T)/T$. The particle diameters inferred from these best fits according to Eq. (7) and those measured by electron microscopy are, respectively, (a) fit: $2a = 0.0975$ μm (measured: $2a = 0.104 \pm 0.005$ μm); (b) 0.113 μm (0.119 ± 0.005 μm); (c) 0.1205 μm (0.1210 ± 0.005 μm).

suming an exponential relaxation of the density matrix after a perturbation of the Hamiltonian. One finds in this way an expression for T_d^{-1} very similar to (3):

$$T_d^{-1} = 2\int_0^\infty dt \langle \vec{\Omega}(0) \cdot \vec{\Omega}(t) \rangle$$
$$\times \exp(-t/T_2)\,dt. \qquad (8)$$

By use of the expression of this Laplace transform given by the modern theory of rotational Brownian motion,[6] one obtains for a single sphere of density ρ in a fluid of density ρ'

$$T_d^{-1} = 6D_0/\{1 + \alpha/15 + \gamma/3(1+\sqrt{\gamma})\} \qquad (9)$$

with $\alpha = \rho a^2/\eta T_2$ and $\gamma = \rho' a^2/\eta T_2$.

The term involving α originates from the inertia of the sphere. It is the inertial effect of the surrounding fluid which results in the term involving γ and correlatively to a long-time tail for $\langle \vec{\Omega}(0) \cdot \vec{\Omega}(t) \rangle$ characterized by a $t^{-5/2}$ asymptotic decay. Therefore, the dipolar relaxation can be used to detect inertial effects if large enough values of α and/or γ are achieved. In our case, the actual figures for α and γ are, however, too small ($\alpha \approx \gamma \approx 10^{-3}$ for $a \approx 0.1$ μm) to introduce any detectable correction to relation (3).

In conclusion, we have shown that the nuclear di-

polar relaxation provides a powerful means for investigating rotational Brownian motion. We have used it to check quantitatively the basic laws of rotational Brownian motion for spherical objects, namely the dependence of the diffusion constant on particle size and on the viscosity of the fluid. Our results are furthermore consistent with recent theories of hydrodynamic interactions at finite concentrations.

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