Jarenwattananon and Bouchard Reply: We thank Lisý and Tóthová (LT) [1] for drawing our attention to a sign error in Eq. (10) in [2]. The second term in the curly braces should be preceded by a minus sign; i.e., the right-hand side should read $kT/M\{[\gamma/(m\zeta_-\zeta_+)] - [1/(\zeta_+ - \zeta_-)] \times \{[1 - (\gamma/m\zeta_+)]e^{-\zeta_+ t} - [1 - (\gamma/m\zeta_-)]e^{-\zeta_- t}\}\}$. This error is typographical and was not carried over to the remaining analysis. The conclusion of the paper remains the same.

It is possible that this typographical error in Eq. (10) of [2] led LT to dispute the sign in the signal decay function. Substitution of the position autocorrelation function (PAF), without the sign typo, in Eq. (3) of [2] and integration yields $\ln S(t) = -\frac{\gamma_n^2 g^2 kT}{M(\zeta_+ - \zeta_-)}[(\zeta_+^{-2}(1 - \frac{\gamma}{m\zeta_+}) - \zeta_-^{-2}(1 - \frac{\gamma}{m\zeta_-}))t - \zeta_+^{-3} \times (1 - \frac{\gamma}{m\zeta_+})(1 - \exp(-\zeta_+ t)) + \zeta_-^{-3}(1 - \frac{\gamma}{m\zeta_-})(1 - \exp(-\zeta_- t))]$. In Ref. [2] it is assumed that $M \gg m$ (strongly overdamped regime). Both limits $\gamma t/m \ll 1$ and $\gamma t/m \gg 1$ yield a negative sign: when $\gamma t/m \ll 1$, $\exp(-\zeta_+ t) \to 1$ and $\exp(-\zeta_- t) \to 1$, all terms without an explicit time dependence cancel out, leaving $\ln S(t) = -[\gamma_n^2 g^2 kT/M(\zeta_+ - \zeta_-)] \times \{\zeta_+^{-2}[1 - (\gamma/m\zeta_+)]t - \zeta_-^{-2}[1 - (\gamma/m\zeta_-)]t\} = (-\gamma_n^2 g^2 \kappa t)$ and we obtain Eq. (13). When $\gamma t/m \gg 1$, $\exp(-\zeta_+ t) \to 0$ and $\exp(-\zeta_- t) \to 0$. Even in that limit, we also obtain Eq. (13) because all terms without an explicit time dependence only result in an overall scaling factor. In both cases, the sign in the exponential term is still negative, i.e., $S(t) \propto \exp(-\gamma_n^2 g^2 \kappa t)$.

Our greatest point of contention is that the "corrected" theory proposed by LT based on mean-squared displacement (MSD) and standard Langevin equation (SLE) contradicts the experiments in [2]: (i) the temperature dependence $T^{1/6}$ has a different sign and magnitude; (ii) their predicted linewidth increases with T.

In the Einstein-Fick limit, replacing the PAF with the MSD is justifiable; i.e., the approximation $\langle x(t)x(0)\rangle \approx x(t)x(t)\rangle = 2Dt$ can be made. Gases fall outside this limit and require a model for $\langle x(t)x(0)\rangle$ that captures the rapid back-and-forth motion of gas molecules which cause the nuclear spins to experience the average magnetic field across the sample over the time scale of the measurement. Since both the NMR observation and dwell times are much longer than the average time between molecular collisions, substantial motional averaging in the magnetic-field gradient takes place leading to a line narrowing effect with temperature. For methane gas at 1 atm and 298 K, $\sim 10^4$ collisions occur on the NMR time scale (dwell time, $\sim 1 \mu$s).

To describe gas self-diffusion we invoked a generalized Langevin equation (GLE). LT's claim that GLE cannot be used because "in gases the memory in the particle dynamics is of low significance" is contrary to the findings of other groups that have performed atomistic calculations [3,4]. The memory functions for gases and liquids both decay on a fairly similar time scale determined by the details of the intermolecular potential. The most significant difference between memory kernels for liquids vs gases is the amplitude of the kernel, not its lifetime.

We note that the GLE is a mere restatement of Newton's laws of motion and is therefore completely general, provided that an adequate memory kernel is used. LT assert that the SLE should be used, citing [5], which in turn cites Langevin [6]. However, Langevin's paper deals with large spherical Brownian particles on the surface of a liquid. There, memoryless forces are justified because the individual collisions of the liquid solvent are much faster than the dynamics of the Brownian particle. For gas self-diffusion, however, the dimensions of the diffusing particle are identical to those of the fluid particles. In that case it is more realistic to use a frictional force that is nonlocal in time. While better choices surely exist, the exponential memory kernel is the simplest model available for describing molecular motion. Our variable-temperature linewidth measurements [2] show that $\Gamma(t) = (\gamma^2/m)\exp(-\gamma t/m)$ adequately captures the temperature dependence. A possible improvement could be to modify the kernel to $\Gamma(t) = \varphi(\rho)\exp(-t/\tau_0)$, where τ_0 depends on the intermolecular potential (in Refs. [3,4] τ_0 is on the order 0.03–0.06 ps) and φ increases with fluid density ρ. Both τ_0 and $\varphi(\rho)$ would depend on temperature and could be obtained from atomistic simulations.

LT object to our use of the PAF, calling it "ill defined," citing Ref. [20] from our paper. However, Ref. [20] does not state that the PAF is ill defined; their concern has to do with the boundedness of the position and velocity processes. In our experiment, molecular positions are bounded by the walls of the NMR tube (4.24 mm i.d.). Unbounded velocities are not statistically probable at finite temperatures. Thus, there are no divergences present. Even if there were no bounding walls, our PAF [Eq. (11)] still decays to zero, as would be expected in the long time limit where correlations are lost. We note that even if a divergence with t existed in the PAF, Eq. (3) would still lead to signal decay.

Finally, we provide validation of our model via an alternative experiment first described in Ref. [7]. Our signal decay function $\exp(-\gamma_n^2 g^2 \kappa t)$, whose argument depends on the first power of time, implies that shortening the interpulse spacing in a CPMG experiment [8,9] should not eliminate the decay from diffusion in field inhomogeneities. The signal decay after application of a CPMG sequence with n echoes leads to the following expression: $S(2n\tau) = \exp(-2n\tau/T_2)\exp[-\gamma^2 g^2 \kappa(2n\tau)]$, where τ is the interpulse spacing. Taking the limit $\tau \to 0$ with a fixed total time $2n\tau$ does not eliminate the second term describing inhomogeneous-field signal decay (g^2 term). In other words, for a gas the T_2 relaxation time does not converge to the same value in the limit of short echo spacing. In contrast, for liquids it is well known that T_2 converges to the same value in the limit $\tau \to 0$ irrespective
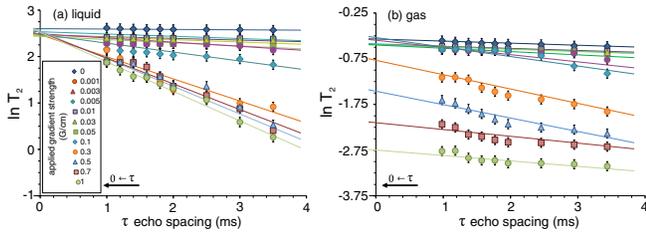
FIG. 1. T_2 relaxation times from CPMG experiment of tetramethylsilane (TMS) as a function of echo spacing (τ) in an inhomogeneous field (applied magnetic field gradient, G/cm). (a) As predicted by traditional NMR theory, in liquid TMS, T_2 times converge to the same value as echo spacing approaches zero. (b) In gaseous TMS, T_2 times do not converge to the same value as the echo spacing approaches zero. The legend of (a) also applies to (b).

of the value of g [8–11]. This prediction is verified experimentally (Fig. 1), further validating our model.

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