Comment on "Pressure dependence of wall relaxation in polarized ^{3}He gaseous cells"

B. Saam,[1,*] A. K. Petukhov,[2] J. Chastagnier,[2] T. R. Gentile,[3] R. Golub,[4] and C. M. Swank[4]
[1]*Department of Physics and Astronomy, University of Utah, Salt Lake City, Utah 84112 USA*
[2]*Institute Laue-Langevin, 38042 Grenoble Cedex, France*
[3]*National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899, USA*
[4]*Physics Department, North Carolina State University, Raleigh, North Carolina 27695, USA*
(Received 24 September 2011; published 26 April 2012)

Zheng *et al.* [Zheng, Gao, Ye, and Zhang, Phys. Rev. A **83**, 061401(R) (2011)] have measured a strong linear pressure dependence of the nuclear relaxation rate of ^{3}He in glass cells typically used to generate and/or store polarized ^{3}He at room and cryogenic temperatures. Their interpretation is that this linear dependence is a general characteristic of paramagnetic wall relaxation, and they offer a theoretical explanation of the effect based on diffusion theory in the bulk with an incorrect boundary condition. We question the physical basis of the boundary condition and suggest some alternate explanations of the observations. Numerous previous studies support a broadly valid pressure-independent model for wall relaxation.

DOI: 10.1103/PhysRevA.85.047401 PACS number(s): 33.25.+k, 51.20.+d, 75.70.Rf, 82.65.+r

I. INTRODUCTION

The central claim of the paper by Zheng *et al.* [1] is that the relaxation rate of nuclear spin-polarized ^{3}He in glass cells depends linearly on the gas pressure at constant temperature. A further claim is that this linear dependence results from diffusive transport of polarized ^{3}He atoms to the cell wall. The authors' theoretical treatment of this relaxation is physically implausible: the characteristic time scale for diffusion across their cells is much shorter than the measured longitudinal nuclear relaxation time T_1, which means that diffusion can play no role in conventional wall relaxation. In addition, their claims would contradict many previous studies over decades that either demonstrate or rely on the assumption that wall relaxation under most circumstances is density independent [2–9] . The physical reasons for the usual pressure independence of wall relaxation are well known to the community and indeed are presented in the discussion of Eq. (1) of Zheng *et al.*:

$$\frac{1}{T_1} = \frac{\mu \bar{v} S}{4V}, \tag{1}$$

where S/V is the surface-to-volume ratio of the cell, $\bar{v}$ is the rms thermal velocity of ^{3}He atoms, and μ is the depolarization probability per wall collision. The point is that the number of wall collisions per particle per second for the entire ensemble is independent of pressure [10]; hence, so is the ensemble average wall depolarization rate. This only breaks down when the depolarization is so strong that it depletes the polarization density near the walls. Zheng *et al.* [1] seek to add a diffusion-dependent component to the relaxation given by Eq. (1), despite the fact that their polarization cells are demonstrably in the weak depolarization limit $\mu \ll 1$. We provide intuitive and formal arguments for the correct handling of diffusion, review the assumptions for the result in Eq. (1), propose possible alternative explanations of the observed results, and review relevant historical results.

II. DIFFUSION EQUATION ANALYSIS

Zheng *et al.* [1] present an explanation of their result based on the diffusion equation [their Eq. (3)], with the ill-posed boundary condition given by their Eq. (5). The boundary condition as stated by Zheng *et al.* [1] is dimensionally incorrect, given that they identify their parameter α to be the probability of polarization loss at the surface. According to standard diffusion theory the correct boundary condition is

$$D \frac{\partial \rho(r,t)}{\partial r}\bigg|_{r=R} = -\frac{\bar{v}}{4}\mu \rho(r,t), \tag{2}$$

where $\rho(r,t)$ is the number density of polarized ^{3}He and D is the diffusion constant. (For example, see Eq. (10) of Ref. [11]). For a discussion of the boundary condition [Eq. (2)] in relation to the diffusion limit of various kinds of random walks see Ref. [12].

Considering the diffusion theory analysis for a spherical cell to first order in the dimensionless parameter $\beta = \mu \bar{v} R/(4D)$, where R is the radius of the cell, the eigenvalue solutions to this problem are $x_k^2 \approx 3\beta + k\pi$ ($k = 0,1,2,3,\ldots$). For weak relaxation ($\beta \ll 1$), the solution for the lowest order mode yields $1/T_1 = x_0^2 D/R^2 = 3\mu\bar{v}/4R$, which is on the order of μ/τ_b, where $\tau_b = R/\bar{v}$ is the time for a ballistically moving particle to traverse the cell. Hence the relaxation time is independent of pressure unless β approaches unity. For $\beta \gg 1$, a graphical solution yields $x_0 \approx \pi$, yielding $T_1 \approx \tau_d < 1$ s compared with ≈20 h for their cell filled with 1 bar ^{3}He, where $\tau_d = R^2/(\pi^2 D)$ is the time constant for the first diffusion mode. If the observed T_1 is much larger than τ_d, then the theory predicts it will be independent of pressure (for a uniform surface).

Additional insight comes from the idea that if two serial processes are required to cause relaxation, then the characteristic times for these processes are added together to yield T_1 [3]. In this case, the typical ^{3}He atom first diffuses to the wall taking a time τ_d. Once near the wall, the characteristic relaxation time is $4V/\mu\bar{v}S$. The measured relaxation time T_1 for the cell is then given by $T_1 \approx \tau_d + 4V/\mu\bar{v}S$. The physics of gas-phase relaxation comes down to the relative size of these two terms and the size of μ. Evaluation of this expression

*saam@physics.utah.edu

 ©2012 American Physical Society

for the conditions of the cells in Ref. [1] yields a plot of the variation of T_1 with μ similar to that shown in Appendix A of Ref. [2]. Such a plot illustrates that the pressure does not affect T_1 unless μ is so large that T_1 becomes comparable to the diffusion time.

III. PRESSURE-DEPENDENT RELAXATION

The result in Eq. (1) of Zheng *et al.* [1] rests on three important assumptions: (i) the wall interactions have a range much shorter than the mean free path λ of the atoms; (ii) the relaxation sites on the wall have a very small occupation probability; and (iii) the wall interactions are everywhere weak, i.e., $\mu \ll 1$ and many wall collisions are required to fully depolarize a spin [2]. The above assumptions are broadly valid, particularly for conventional sealed glass cells. For paramagnetic relaxation sites, assumption (i) is easily satisfied: the range of the wall interaction is perhaps a few tenths of a nanometer, whereas the mean free path at 1 bar is >100 nm and even longer at lower pressures. Given the extremely short duration ($\leqslant$1 ps) for wall collisions, assumption (ii) is almost certainly satisfied for any reasonable gas density. For the cells in Ref. [1], $T_1 \gg \tau_d$ is always satisfied.

Assumption (iii) can be violated if the depolarization is so strong that it depletes the polarization density near the walls. This suggests a possible explanation of the observations of Zheng *et al.* [1]. Localized regions of the surface with a high depolarization probability would deplete the local polarization density resulting in a linear pressure dependence, while, since they cover only a fraction of the surface, the resulting T_1 would not be too short. In the experiment the cells used at room temperature were made of Rb-coated Pyrex and were connected to an O-ring valve through a 1.5-mm-inner-diameter Pyrex capillary tubing. These attachments may be acting as a localized region with very high depolarization rate while the rest of the cell has a negligible effect on the apparent relaxation rate. In this case the rate of diffusion through the capillary to the valve can directly affect the relaxation rate, and Zheng *et al.* [1] do not show definitively that this diffusion can be neglected in their cells. Jacob *et al.* [13] treated this problem with the simplifying assumptions that the valve materials have $\mu = 1$ and the capillary walls have $\mu \ll 1$. They found that the contribution to relaxation from the capillary is given by

$$\left(\frac{1}{T_1}\right)_{\text{cap}} = \frac{\pi r^2 D}{V L}, \tag{3}$$

where r and L are the capillary radius and length. The prediction of Eq. (3) for the cells in Ref. [13] was found to be in approximate agreement with the capillary relaxation by positioning a bead of Rb metal over the capillary opening. Equation (3) predicts T_1 to be proportional to pressure through the inverse pressure dependence of D. Not only is this the same pressure dependence observed in Ref. [1] at low pressure, but if we take a typical value (0.15 bar) in the middle of the linear pressure range for the Rb-coated cell in Fig. 2 of Ref. [1], using $r = 0.75$ mm, $L = 18$ cm, $V \approx 50$ cm^3, and $D \approx 12$ cm^2/s, we estimate $(T_1)_{\text{cap}} \approx 1.2$ h. The measured T_1 at this pressure is $\approx$2 h, meaning that it is very plausible for relaxation due to the capillary and valve to contribute significantly to or even dominate the relaxation, even if the valve materials are less than perfectly relaxing.

We have carried out a finite-element simulation of the problem using the geometry used in Ref. [1] at $T = 4.2$ K (including the restriction in the tube at the entrance to the cell) and the diffusion constant obtained from the viscosity, and we have obtained results consistent with the measurements if we allow for the temperature change along the capillary tube. At low pressures where the relaxation time is driven by the transport of the depolarized gas through the tube, a linear pressure dependence is observed. Furthermore the relaxation time can be shortened by moving the surface impurity in the tube closer to the cell, while maintaining the linear pressure dependence. At high pressures the transport from the impure surface is no longer a dominant factor and the wall relaxation in the cell becomes the dominant source of relaxation. At these pressures virtually no depolarized gas is transported from the impure surface to the bulk and no pressure dependence is seen.

Other explanations are possible. While gradient relaxation at the high pressures used in their experiment also give $T_1 \propto p$, [14], Zheng *et al.* [1] have ruled out static gradients as a possible cause of the observed behavior. However there is the possibility that inhomogeneous ac fields, which result in a similar pressure dependence of T_1 [15], may be playing a role. As pointed out by Zheng *et al.* [1] pressure dependence was reported in the low temperature experiments in their Ref. [8] and ascribed to a pressure dependence of μ, associated with an adsorbed phase on the surface.

Previous work on cells with multidomained ferromagnetic relaxation sites [6] showed that T_1 can in this case depend on the diffusion coefficient. Zheng *et al.* [1] suggest that the departure from linear dependence at high pressures may be due to ferromagnetic sites having the opposite pressure dependence, as observed in Ref. [6]. However, the cells in Ref. [6] exhibited this pressure dependence only after being exposed to magnetic fields on the order of 1 T or more; it disappeared for cells that had been "degaussed." Zheng *et al.* [1] are clear that their cells have never been exposed to high fields and further state that ferromagnetic sites cannot be the dominant cause of relaxation in their cells, despite the fact that they later offer this very explanation for the flattening of their T_1 curves at high pressures.

IV. DISCUSSION OF PAST RESULTS

Zheng *et al.* [1] point out that their results are inconsistent with past results for low-pressure metastability-exchange optical pumping (MEOP) cells, arguing that relaxation in those cells is likely dominated by other mechanisms, such as relaxation to ferromagnetic wall sites and dipole-dipole relaxation that occurs in ^{3}He-^{3}He collisions. First, dipole-dipole relaxation is given by $800/p$ h [4], where p is the pressure in bar, hence at pressures below 10 mbar this contribution would be greater than 80 000 h. Second, ferromagnetic relaxation appears to manifest in just a few special cases and is linear in pressure; it is thus highly implausible that it plays much of a role in the decades of past results that are entirely consistent with pressure-independent wall relaxation. It is worth recounting some of these results, as they cover a wide

range of cell constructions for both MEOP and spin-exchange optical pumping (SEOP) over a broad range of pressures.

Fitzsimmons *et al.* [3] found no systematic dependence of the relaxation time on ^{3}He density for the 2.7 to 27 mbar pressure range at room temperature. These studies included bare Corning 7740 (Pyrex) [16] and aluminosilicate glass cells; the Pyrex cells had relaxation times of ≈4 h at room temperature. One of us (T.R.G.) has observed comparable relaxation times in both sealed Pyrex MEOP cells at pressures on the order of 1 mbar as well as in valved Pyrex storage cells (equipped with suitable diffusion-restricted capillaries) at pressures between 0.3 and 1 bar [17]. Indeed, in Ref. [17] no pressure dependence was observed for either Pyrex or aluminosilicate glass storage cells for pressures between 0.3 and 1 bar. Heil *et al.* [5] studied sealed cells at pressures of 8 mbar and 2.3 bar, for both bare and metal-coated Pyrex and aluminosilicate glass; they demonstrated the clear advantages of metal coatings, especially for Pyrex. However, they observed no systematic difference, for the same coating and glass, between the two dramatically different pressures. Andersen *et al.* [18] have observed $T_1 \approx 8$ h at pressures of ≈1 mbar in the ILL optical pumping station [18]. More recently, one of us (A.P.) has measured the T_1 of a valved, 6-cm-diameter Pyrex cell at several pressures between 0.15 and 4.0 bar and found all the T_1 values to be within ±20% of a value of 7.5 h.

Newbury *et al.* [4] constructed a remarkable series of aluminosilicate cells containing Rb for SEOP, in which wall relaxation was almost completely suppressed. This allowed them to compare the pressure dependence of relaxation for cells filled to pressures between 1 and 4 bar to the linear dependence expected from their calculation of dipole-dipole relaxation. No other source of pressure dependence was expected or included in their analysis. Tests of the dipole-dipole calculation have been extended down to 0.5 bar [19], and the best cells show the pressure-dependent limit expected for dipole-dipole relaxation. In summary, no evidence has ever been shown for any pressure dependence to ^{3}He relaxation except for that expected from dipole-dipole relaxation [4] (primarily at high pressures), static [14] and ac [15] magnetic field gradients (primarily at low pressures), or magnetized cells [6,20] (where invoking ferromagnetism is justified).

Hence, it appears that the observations of Zheng *et al.* [1] do not represent a general property of wall-induced relaxation but are the result of the properties of their individual cells and/or other details of their experiment.

V. CONCLUSION

Whatever the complexities of the experimental situation, the authors' claim that α in their Eq. (5) is independent of D has no physical basis. As the equation is written α has the units of inverse length. With the only physical length in the bulk being the mean free path of the diffusing particles, we are back to the diffusion constant, $D \sim \lambda\bar{v}$ (λ being the mean free path for collisions.) There is no justification for setting the current proportional to the gradient other than diffusion theory. The application of the diffusion theory in their Eqs. (3) and (6) and the denial of its applicability in Eq. (5) are inconsistent. Although Zheng *et al.* dismiss capillary relaxation as negligible, previous experimental results and our simulations show that it is the most likely explanation for the observed linear pressure dependence in Ref. [1].

[1] W. Zheng, H. Gao, Q. Ye, and Y. Zhang, Phys. Rev. A **83**, 061401(R) (2011).
[2] R. L. Garwin and H. A. Reich, Phys. Rev. **115**, 1478 (1959).
[3] W. A. Fitzsimmons, L. L. Tankersley, and G. K. Walters, Phys. Rev. **179**, 156 (1969).
[4] N. R. Newbury, A. S. Barton, G. D. Cates, W. Happer, and H. Middleton, Phys. Rev. A **48**, 4411 (1993).
[5] W. Heil *et al.*, Phys. Lett. A **201**, 337 (1995).
[6] R. E. Jacob, S. W. Morgan, B. Saam, and J. C. Leawoods, Phys. Rev. Lett. **87**, 143004 (2001).
[7] B. Chann, I. A. Nelson, L. W. Anderson, B. Driehuys, and T. G. Walker, Phys. Rev. Lett. **88**, 113201 (2002).
[8] B. N. Berry-Pusey, B. C. Anger, G. Laicher, and B. Saam, Phys. Rev. A **74**, 063408 (2006).
[9] B. C. Anger *et al.*, Phys. Rev. A **78**, 043406 (2008).
[10] F. Reif, *Fundamentals of Statistical and Thermal Physics* (McGraw-Hill, New York, 1965), p. 272.
[11] D. S. Grebenkov, Rev. Mod. Phys. **79**, 1077 (2007).
[12] R. Erban and S. J. Chapman, Phys. Biol. **4**, 16 (2007).
[13] R. E. Jacob, S. W. Morgan, and B. Saam, J. Appl. Phys. **92**, 1588 (2002).
[14] G. D. Cates, S. R. Schaefer, and W. Happer, Phys. Rev. A **37**, 2877 (1988).
[15] G. D. Cates, D. J. White, T. R. Chien, S. R. Schaefer, and W. Happer, Phys. Rev. A **38**, 5092 (1988).
[16] Corning Glass, Corning, NY 14831. Certain trade names and company products are mentioned in the text or identified in an illustration in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.
[17] T. R. Gentile *et al.*, J. Res. Natl. Inst. Stand. Technol. **106**, 709 (2001).
[18] K. H. Andersen *et al.*, Physica B **356**, 103 (2005).
[19] W. C. Chen *et al.*, J. Phys.: Conf. Ser. **294**, 012003 (2010).
[20] J. Schmiedeskamp *et al.*, Eur. Phys. J. D **38**, 445 (2006).