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

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W. Zheng *et al.* [Phys. Rev. A **83**, 061401(R) (2011)] measure under certain conditions a linear pressure dependence of the wall-induced nuclear relaxation rate of ^{3}He in glass cells typically used to generate and/or store hyperpolarized ^{3}He. Their interpretation is that this linear dependence is a general characteristic of paramagnetic wall relaxation, regardless of the relationship between the diffusion time τ_d across the cell and the longitudinal nuclear relaxation time T_1. The authors' proposed modification of the polarization diffusion equation to account for this dependence cannot be valid for $T_1 \gg \tau_d$, which holds for all of their measurements. Numerous previous studies support a broadly valid pressure-independent model for wall relaxation. The likely explanation for the linear dependence observed by the authors is diffusion through a capillary to a refilling valve that has a much higher probability per collision to relax ^{3}He.

I. INTRODUCTION

The central claim of the paper by W. 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 ^{3}He atoms to the cell wall. Were they valid, these 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 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. While the experimental data presented by the authors of [1] do indeed show the linear dependence (at all but the highest pressures measured) and do appear to be sound, the interpretation of these data as evidence for the above claims is made with insufficient regard for the possibility of relaxation due to transport of ^{3}He down the capillary tube that connects the cell to a much more relaxive refilling valve. This unconventional "capillary" relaxation should depend on pressure in the way observed in [1].

The authors first present in Eq. (1) of [1] the widely-assumed standard model for ^{3}He wall relaxation in glass cells due to paramagnetic surface impurities:

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

where S/V is the surface-to-volume ratio of the cell, $\bar{v}$ is the rms thermal velocity of ^{3}He atoms, and α is the depolarization probability per wall collision. This model rests on several 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., $\alpha \ll 1$ and many wall collisions are required to fully depolarize a spin [2]. The relaxation rate thus depends only on the rate of wall collisions, which is independent of collisions between atoms [10]. This is operationally equivalent to observing $T_1 \gg \tau_d$, where $\tau_d \approx R^2/D$ is the characteristic diffusion time across the cell.

The above assumptions are broadly valid, making Eq. (1) a *complete description* of wall relaxation in most cases, particularly for conventional permanently sealed glass cells. As discussed below, assumption (iii) can be violated for valved cells due to capillary relaxation; for the moment we set aside this possibility and assert that these assumptions are otherwise very well satisfied for the cells in [1]. 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. Contrary to what is implied in [1], ballistic collisions between atoms and the wall are entirely responsible for wall relaxation due to paramagnetic impurities. Previous work on cells with multi-domained ferromagnetic relaxation sites [6] showed that T_1 can in this case depend on the diffusion coefficient, because these sites have an in-

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teraction range that violates assumption (i). Given the extremely short duration ($\leq$ 1 ps) for wall collisions, assumption (ii) is almost certainly satisfied for any reasonable gas density. For the 45 mm diameter spheres in [1], T_1 is measured in hundreds of minutes at the highest pressures, where $\tau_d \approx 30$ s at most. At the lowest pressures, where T_1 is at least several minutes, τ_d is a few seconds at most. Hence, $T_1 \gg \tau_d$ is always satisfied. Ignoring the capillary, the measured relaxation times T_1 in [1] should follow Eq. (1) and, contrary to the authors' assertion, cannot depend on diffusion across the cell.

The formulation of the diffusion equation in Eqs. (3)-(5) of [1] for the polarization $\rho(r,t)$ is incorrect for the conditions specified. The boundary condition for $\partial\rho/\partial r$ in Eq. (5) of [1] is not dimensionally correct and is in any case ill-defined at $r = R$. The solution in Eq. (6) of [1] leads to a significant value for $\partial\rho/\partial r$ across the cell, which cannot be the case for $T_1 \gg \tau_d$. The nuclear spins slowly relax as they diffuse around the cell, but there is no polarization gradient except for very close to the walls. The characteristic diffusion time R^2/D cannot appear in the solution because relaxation occurs (demonstrably) on a much slower time scale. The wall relaxation would be more properly accounted for as a source term $Q(R) = -\rho(R,t)/T_1$ added to the left side of Eq. (3) of [1], with T_1 given by Eq. (1).

II. SOURCES OF PRESSURE-DEPENDENT RELAXATION

We now treat the introduction of a valve to the cell, which can cause assumption (iii) above to be violated if the valve materials have α on the order of unity, requiring only one or a few collisions to relax ^{3}He spins. This situation is often addressed, as was done in [1], by introducing a capillary tube that limits the flux of atoms to the valve from the main body of the cell. In this case the rate of diffusion through the capillary to the valve can directly affect the relaxation rate, and the authors of [1] do not show definitively that this diffusion can be neglected in their cells. Jacob *et al.* [11] treated this problem with the simplifying assumptions that the valve materials have $\alpha = 1$ and the capillary walls have $\alpha \ll 1$. They found that the contribution to relaxation from the capillary is given by:

$$\left(\frac{1}{T_1}\right)_{cap} = \frac{\pi r^2 D}{VL}, \qquad (2)$$

where r and L are the capillary radius and length. The prediction of Eq. (2) for the cells in [11] was found to be in approximate agreement with the capillary relaxation by positioning a bead of Rb metal over the capillary opening. Equation (2) 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 [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 [1], using $r = 0.75$ mm, $L = 18$ cm, $V \approx 50$ cm^3, and $D \approx 12$ cm^2/s, we estimate $(T_1)_{cap} \approx 1.2$ h. The measured T_1 at this pressure is ≈ 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.

To explain the flattening of their relaxation time data at high pressure in Fig. 2 of [1], the authors state,"This clearly indicates that some other relaxation mechanisms, which are negligible at low pressure, become important at high pressure, since the paramagnetic relaxation becomes less pronounced with increasing pressures." In fact, a more reasonable conclusion is that the flattening is due to the decreasing contribution from some pressure dependent source, such as diffusion to a relaxing valve and/or capillary, leaving only the pressure-independent paramagnetic relaxation given by Eq. (1) apparent at high pressures. The authors further suggest that the departure from linear dependence at high pressures may be due to ferromagnetic sites having the opposite pressure dependence, as observed in [6]. However, the cells in [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." The authors of [1] are clear that their cells have never been exposed to high fields and, in spite of later offering this explanation for the flattening of the T_1-curve at high pressures, state that ferromagnetic sites cannot be the dominant cause of relaxation in their cells. Some light might have been shed on these questions had the authors undertaken additional experiments in which the capillary dimensions were changed, cells were exposed to higher magnetic fields, or a series of otherwise identical sealed cells having different pressures had been studied.

We have restricted our discussion to the room-temperature measurements in [1]. The data at 4 K are much more difficult to assess and interpret, and we would need to know more about the details of the experiment. Indeed, if one assumes that all the helium in these experiments moves through the cell and capillary by diffusion at 4 K, then the model in Eq. (2) results in values of $(T_1)_{cap}$ that are much too long to explain the data in a way similar to the room-

temperature data. On the other hand, the volume of capillary tubing connecting the cell to the valve in these experiments is about four times larger than the volume of the nominal cell. It is not clear from [1] what fraction of the capillary tubing is immersed in liquid helium; diffusion at room temperature will be faster. Finally, one cannot discount the possibility, especially with such a significant temperature gradient across the cell, that convection is playing a major role in transporting gas from the main body of the cell through the capillary and to the valve. Coupled with the fact that only one of the four data sets in Fig. 1 of [1] has as many as three points, it would not appear safe even to conclude that the pressure dependence is generally linear in this experiment, let alone that it could be characterized with the diffusion model proposed by the authors.

III. DISCUSSION OF PAST RESULTS

The authors of [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 $800/p$ hours [4], where p is the pressure in bar, hence at pressures below 10 mbar this contribution would be greater than 80,000 hours. 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 role in the decades of past results that are entirely consistent with pressure-independent wall relaxation. It is worth recounting some of these previous 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 mbar to 27 mbar pressure range at room temperature. These studies included bare Corning 7740 (Pyrex) [12] and aluminosilicate glass cells; the Pyrex cells had relaxation times of $\approx$ 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 valved Pyrex storage cells (equipped with suitable diffusion-restricted capillaries) at pressures between 0.3 bar and 1 bar [13]. Indeed, in [13] 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.

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 bar 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 [14], 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 (primarily at high pressures), magnetic field gradients (primarily at low pressures), or magnetized cells (where invoking ferromagnetism is justified). Except for the special cases of magnetized cells discussed in [6] and [15] no previous studies have even considered such a dependence for wall relaxation due to the consideration discussed above, nor has past work shown any justification for invoking ferromagnetic relaxation. Even if the theoretical analysis of diffusion were correct and even if it proved that diffusion to a relaxing capillary is not the operative parameter in their experiments, it would fall upon the authors of [1] to provide much more substantial reanalysis of a half century of cell results.

IV. CONCLUSION

In summary, the authors of [1] do not make a convincing case for their central claim that nuclear spin relaxation of ^{3}He due to wall collisions is linearly dependent on gas pressure due to diffusive transport of atoms to the cell walls. Although the exact nature of wall relaxation is still poorly understood, there is an abundance of previous work and solid physical reasoning to suggest that wall relaxation due to interaction with paramagnetic impurities is independent of gas pressure at constant temperature. The main problem with the authors' claim is that it is general, pertaining both to weak and strong relaxation sites. However, in the former case ($\alpha \ll 1$) it is inappropriate to treat relaxation by diffusive transport, because the measured relaxation time T_1 far exceeds the characteristic diffusion time τ_d across

the cell. In the latter case ($\alpha \approx 1$), depending on the relative size and potency of strongly interacting sites and on whether some effort has been made to isolate these sites from the main body of the cell (e.g., with an intervening capillary in the case of a relaxive valve), relaxation may be diffusion-limited. Although the authors dismiss capillary relaxation as negligible, it is the most likely explanation for the observed linear pressure dependence in [1]. Were it possible to construct a series of sealed cells having the same small value of $\alpha \ll 1$ but with different pressures, the linear dependence seen in [1] would almost certainly disappear.

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