

## Comment on “Enhanced polarization and mechanisms in optically pumped hyperpolarized $^3\text{He}$ in the presence of $^4\text{He}$ ”

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(Received 5 December 2012; published 24 July 2013)

Chen *et al.* [[Phys. Rev. A \*\*81\*\*, 033422 \(2010\)](#)] claim that adding  $^4\text{He}$  to spin-exchange optical pumping (SEOP) cells confines  $^3\text{He}$  atoms to a diffusion-limited region, which effectively reduces the wall relaxation factor  $X$ . Here  $X$  is a phenomenological parameter used to characterize typical SEOP cells; it quantifies the observation that the measured linear slope of the relaxation rate with alkali-metal-atom density exceeds the spin-exchange rate. In addition they claim to demonstrate that magnetic-field gradients cause a diffusive motion of  $^3\text{He}$ . We argue that these claims and other central conclusions drawn by Chen *et al.* [[Phys. Rev. A \*\*81\*\*, 033422 \(2010\)](#)] are inconsistent with the physics of diffusion or should not be made from the data as presented. We also draw attention to several additional issues associated with the results, analysis, and presentation of data in Chen *et al.* [[Phys. Rev. A \*\*81\*\*, 033422 \(2010\)](#)] that confound clear interpretation.

DOI: [10.1103/PhysRevA.88.017401](https://doi.org/10.1103/PhysRevA.88.017401)

PACS number(s): 33.25.+k

### I. INTRODUCTION

In an article reporting on results of spin-exchange optical pumping (SEOP) of  $^3\text{He}$  [1], Chen *et al.* come to several questionable conclusions regarding the effects of magnetic-field gradients and the role of  $^4\text{He}$ . We find issues in their discussion of the physics underlying gas diffusion and spin-exchange optical pumping. In addition, the experimental details and data analysis methods are not described in such a way that a reader can fully understand and interpret the presented results. In this Comment, we identify and briefly discuss some of these issues.

We begin in Sec. II with two claims made by the authors of Ref. [1] that are attributed to implausible mechanisms and for which neither supporting evidence nor arguments are presented. In Sec. III we argue that claims of changes in relaxation rates with added  $^4\text{He}$  or with field homogeneity are not supported by the corresponding data. In addition, we discuss the inconsistent use of presented equations and problematic statements. In Sec. IV we summarize the Comment.

### II. UNPHYSICAL CLAIMS

The first of these claims, highlighted in the Abstract and stated in the Discussion, is that the addition of  $^4\text{He}$  gas to a SEOP cell “confines the  $^3\text{He}$  atoms to a diffusion-limited region, which effectively reduces the wall relaxation factor  $X$ .” Certainly the addition of  $^4\text{He}$  increases the total gas pressure and correspondingly decreases the  $^3\text{He}$  mean-free path. However, wall relaxation is generally independent of pressure [2–4], except for special cases unlikely to be relevant in Ref. [1]. In brief, the characteristic time scales for diffusion in typical SEOP cells are on the order of seconds, whereas,

the time scales for relaxation (including wall relaxation) are on the order of hours. In this context,  $^3\text{He}$  atoms explore the entire cell and, thus, collide with the walls many times before eventually undergoing a spin-flip transition. The rate at which the constituents of any component  $i$  of an ideal gas mixture collide with the walls of a container depends only on the partial pressure  $p_i$ , not the total gas pressure  $p = \sum_i p_i$ . The suggestion made in Ref. [1], that the addition of  $^4\text{He}$  gas to a SEOP cell somehow “confines”  $^3\text{He}$  atoms so as to keep them from interacting with the cell walls, violates this fundamental tenet of kinetic theory.

The second claim, made in the Introduction and the Discussion, is that the authors of Ref. [1] “demonstrate that the gradient field causes a diffusive motion of  $^3\text{He}$ .” This claim is unphysical because the diffusive motion of  $^3\text{He}$  atoms is a stochastic process governed by the temperature of the system, whereas, motion caused by field gradients is deterministic. It is diffusion in the presence of a gradient in the magnetic field  $\mathbf{B}$  that leads to nuclear-spin relaxation [5]. However, there is no evidence (in Ref. [1] or elsewhere) or reason to suspect that those same field gradients cause, enhance, or otherwise influence the random nature of atomic diffusion. Even the (nonrandom, directed) drift of  $^3\text{He}$  atoms driven by the gradient in nuclear magnetic energy is tiny in these experiments. This issue was examined by Torrey in a seminal paper [6,7]. Readers may wish to consult Ref. [8] for an example of a situation in which the forces associated with a magnetic-field gradient are large enough to drive a substantial nuclear magnetization current.

The gradient-induced nuclear relaxation rate is directly proportional to the square of the relative magnetic-field gradient  $G = |\nabla B_\perp|/B$  and is inversely proportional to the total gas pressure  $p$ . Here  $|\nabla B_\perp|$  represents the volume-averaged transverse component of the gradient in the static magnetic field. For the stated conditions of Ref. [1] ( $p$  on the order of

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1 bar and  $B$  homogeneous to one part in  $10^3$  over a  $42\text{-cm}^3$  cell) one expects the time constant for gradient-induced relaxation to be hundreds of hours or more [9], to the extent that the diffusion of  $^3\text{He}$  in the presence of (uncharacterized) field gradients along the fill tube can be ignored. This time scale is orders of magnitude longer than the measured relaxation times reported in Ref. [1].

### III. DATA ANALYSIS AND PRESENTATION

We next consider an important claim made by the authors of Ref. [1] that appears to be inconsistent with their own data. In one set of experiments they report that “the relaxation time  $T_1$  of  $^3\text{He}$  . . . is improved from 2.05 to 2.46 h when the pressure of  $^4\text{He}$  is increased from zero to 1850 torr.” This statement is then used (with no further analysis or commentary) to support the previously discussed implausible claim that “ $^4\text{He}$  can reduce the wall relaxation rate.” In this experiment, the  $^3\text{He}$  pressure was reported to be 600 torr, and the nitrogen pressure was 60 torr, hence, the total gas pressure varied between 660 and 2510 torr as the  $^4\text{He}$  was added.<sup>1</sup> The claim that  $T_1$  is improved is based on the data shown in Fig. 3 of Ref. [1], which shows  $^3\text{He}$  polarization as a function of time. Specifically, the authors of Ref. [1] fit exponential decay curves to the data acquired during the relaxation phase of two of the nine datasets presented in that figure and extract the corresponding time constants: 2.05 and 2.46 h at  $^4\text{He}$  partial pressures of 0 and 1850 torr, respectively. They ignore the remaining seven datasets presented in that figure insofar as their claim of improved  $T_1$  is concerned. We have graphically extracted values for the data plotted in that figure and have analyzed them in the prescribed manner. Our analysis yields decay time constants that accurately duplicate the values of  $T_1$  for the two datasets that were singled out by the authors and yields seven additional values of  $T_1$  that are not mentioned in their paper. Collectively, the nine measured time constants reveal no statistically significant evidence for an increase in  $T_1$  with  $^4\text{He}$  partial pressure. In fact, they are consistent with random scatter about a pressure-independent mean value of  $(2.2 \pm 0.2)$  h. If one were to select two other datasets from among those presented in Fig. 3 of Ref. [1], one might just as well conclude that  $T_1$  is degraded by the addition of  $^4\text{He}$ . To summarize, the data shown in Fig. 3 of Ref. [1] do not support the authors’ associated claim that  $T_1$  is increased through the addition of  $^4\text{He}$ . Instead, they reveal a large degree of scatter in measured relaxation times, which could be indicative of uncontrolled systematic issues. It is noteworthy that the authors of Ref. [1] do not report or discuss uncertainties in measured values, nor do they seem to have investigated the reproducibility of their data. For instance, the  $T_1$  we obtain for the decay at a temperature of  $200^\circ\text{C}$  in Fig. 2 is 1.10 h, half the average of the values in Fig. 3 for a very similar or identical gas pressure. This difference, although much larger than the alleged effect of the added  $^4\text{He}$  on  $T_1$ , is not explained.

These issues lead us to another serious weakness in the documentation of the experiments presented in Ref. [1]: The

<sup>1</sup>Although no specific information is given, we assume that pressures reported in Ref. [1] were measured at room temperature and actually correspond to gas densities in units of cell-filling pressures.

authors do not make clear as to when relaxation at room temperature was measured and when relaxation at optical pumping temperatures was measured. Furthermore, it appears that they may not have employed consistent equations for the interpretation of the temporal behavior of their optical pumping and relaxation data. The time evolution of the nuclear polarization of the  $^3\text{He}$  gas  $P_{\text{He}}$  is derived from the rate equation,

$$\frac{dP_{\text{He}}}{dt} = \gamma_{\text{se}}(P_{\text{Rb}} - P_{\text{He}}) - \Gamma P_{\text{He}}, \quad (1)$$

which links it to the rubidium polarization  $P_{\text{Rb}}$  and the  $^3\text{He}$  relaxation rate (due to all sources except spin exchange)  $\Gamma$ . The spin-exchange rate  $\gamma_{\text{se}}$  is given by  $\gamma_{\text{se}} = \kappa_{\text{se}}[\text{Rb}]$ , where  $\kappa_{\text{se}}$  is the rubidium- $^3\text{He}$  spin-exchange rate coefficient and  $[\text{Rb}]$  is the rubidium density. For optimal optical pumping conditions  $P_{\text{Rb}} \approx 1$ , whereas, in the absence of optical pumping  $P_{\text{Rb}} \approx 0$ .

Experimentally it has been observed [10] that  $\Gamma$  has a component that scales with alkali-metal density, hence, it can be written as  $\Gamma = \Gamma_r + \gamma_{\text{se}}X$ , where  $\Gamma_r$  includes contributions from dipole-dipole relaxation, wall relaxation, gradients, and perhaps other sources, such as diffusion to a relaxing valve. In this formulation the slope of the relaxation rate with rubidium density is given by  $\kappa_{\text{se}}(1 + X)$ , and the limiting  $^3\text{He}$  polarization for  $\Gamma_r = 0$  is given by  $P_{\text{Rb}}/(1 + X)$ . Polarization buildups and decays can be derived from Eq. (1): The steady-state polarization  $P_{\text{He}}^\infty = P_{\text{Rb}}\gamma_{\text{se}}/\Gamma_{\text{He}}$  is asymptotically reached with a rate given by

$$\Gamma_{\text{He}} = (1 + X)\gamma_{\text{se}} + \Gamma_r, \quad (2)$$

and decays to  $P_{\text{He}} = 0$  (when  $P_{\text{Rb}} = 0$ ) clearly occur with the *same* rate. Spin-exchange collisions are present even when  $P_{\text{Rb}} = 0$  and act along with any other depolarization mechanism. Equation (2) is used by Chen *et al.* in their Eq. (5), but it is unclear whether it is applied correctly and consistently in their analysis. In particular, this (correct) expression is inconsistent with Eqs. (2) and (3) of Ref. [1] in which  $X$  is overlooked and  $\Gamma_1$  is not clearly defined. From Eq. (3) of Ref. [1],  $\Gamma_1$  appears to be the polarization decay rate  $\Gamma_{\text{He}}$ , that should contain the same contribution due to spin exchange as the buildup rates in Eqs. (2) and (5) of Ref. [1]. For a set temperature, the rate  $\Gamma_{\text{He}}$  should be the same whether measured during optical pumping or during relaxation with the laser off; if differences are observed, then there may be heating of the cell by the laser, resulting in a change in the rubidium density. It is generally assumed that the only significant temperature dependence in  $\Gamma_{\text{He}}$  is due to the linear dependence on rubidium density through  $\gamma_{\text{se}}$ . Although most SEOP cells show a linear increase in relaxation rate, some evidence for additional temperature dependence attributed to wall relaxation in fused quartz cells has been reported [11]. Additionally, diffusion-related relaxation rates, such as diffusion through a tube to a relaxing valve [12], also vary with the gas temperature.

The authors of Ref. [1] also present a surprising result regarding the effect of changing their magnetic-field homogeneity (see the data and discussion of Fig. 5). They find that an 8.5% decrease in the fractional nuclear magnetic resonance (NMR) frequency width  $\Delta f/f$  yields an increase in the  $^3\text{He}$  polarization from 10% to 19% and an increase in

$T_1$  from 1.82 to 5.75 h. They claim that these data “suggest that the field gradient affects the polarization of both Rb and  $^3\text{He}$  significantly, . . . .” The rubidium polarization is determined by a balance between the optical pumping rate and the rubidium spin relaxation [13] where any rubidium relaxation from a field gradient is negligible. The increase in  $T_1$  could explain the increase in  $^3\text{He}$  polarization, hence, we focus on the relaxation time. The origin of the inhomogeneity and its spatial variations are not specified, but it does not seem to be a controlled applied field gradient that could be adequately characterized by  $\Delta f/f$ . If this were the case, the gradient-induced contribution to the nuclear relaxation rate would scale as  $(\Delta f/f)^2$  [5,9]. The authors do not provide any justification that the large change in  $T_1$  that they observed was due to a change in the field homogeneity, nor that the linewidth of the NMR signal was an accurate characterization of the relevant magnetic-field map. One may, for instance, speculate that gradient-induced relaxation was dominated by the effect of a large local field inhomogeneity at the distal end of the tube connecting the cell to the valve, a region which may lie outside of the homogeneous field region probed by the free induction decay signal. Moreover, depending on the geometry of the connecting tube and on details of local relaxation processes, any relaxation in the valve or in the tube could produce an apparent dependence on pressure.

#### IV. CONCLUSION

In conclusion, we find that Ref. [1] proposes implausible explanations for questionable results and incorrectly applies the basic physics of diffusion and SEOP. Most importantly, the authors of Ref. [1] make unphysical claims regarding the role of pressure in  $^3\text{He}$  relaxation in SEOP cells. Their central claim that “ $^4\text{He}$  gas confines the atoms to a diffusion-limited region which effectively reduces the wall relaxation factor  $X$ ” is inconsistent with the basic physics of diffusion and is in conflict with many other past studies. They present analysis of their data that leads them to conclude that the addition of  $^4\text{He}$  decreases the  $^3\text{He}$  wall relaxation rate, whereas, we find that this analysis may be faulty and/or incomplete. However, our ability to comment on their experiments and analysis is ultimately confounded by incomplete or unclear documentation in their paper. It is critical that any future work in this area be better documented. If pressure-dependent effects are still apparent after a careful and complete analysis (that includes experimental uncertainties), it is incumbent upon the authors of Ref. [1] to thoroughly examine the influence of known mechanisms that might explain their data before invoking anything more dramatic. Finally, any new phenomena proposed must be physically plausible.

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[7] A gradient in magnetic-field strength  $B$  (and, hence, magnetostatic energy  $-\boldsymbol{\mu} \cdot \mathbf{B}$ ) establishes a counterflow of  $^3\text{He}$  atoms in the two spin states. Here  $\boldsymbol{\mu}$  is the  $^3\text{He}$  nuclear magnetic moment. When this gradient is first applied to an ideal gas at temperature  $T$ , the resulting initial drift velocities are  $\mathbf{v}_{\pm}^0 = \pm[D\boldsymbol{\mu}/(kT)]\nabla B$ , where  $D$  is the diffusion coefficient,  $k$  is Boltzmann’s constant, and the subscripts denote the two possible spin orientations with respect to  $\mathbf{B}$ . This counterflow drives gradients in the densities ( $n_+$  and  $n_-$ ) of atoms in the two spin states, which are then opposed by diffusion. In the steady state

this leads to  $\nabla n_{\pm} = \pm n_{\pm} \mathbf{v}_{\pm}^0$ . Evaluating  $|\mathbf{v}_{\pm}^0|$  and  $|\nabla n_{\pm}|/n_{\pm}$  for the conditions of Ref. [1] yields values on the order of  $10^{-14}$  m/s and  $10^{-10}$   $\text{m}^{-1}$ , respectively. These are both exceedingly small by any measure relevant to the experiments described in Ref. [1]. For scale, Earth’s gravitational field produces gradients in the total  $^3\text{He}$  density  $n = n_+ + n_-$  such that  $\nabla n/n \sim 10^{-5}$   $\text{m}^{-1}$  at room temperature.

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