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Propagation of dynamic nuclear polarization across the xenon cluster boundaries: Elucidation of the spin-diffusion bottleneck

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ABSTRACT

Earlier Dynamic Nuclear Polarization (DNP) experiments with frozen xenon/1-propanol/trityl mixtures have demonstrated spontaneous formation of pure xenon clusters above 120 K, enabling spectrally-resolved real-time measurements of ^{129}Xe nuclear magnetization in the clusters and in the surrounding radical-rich matrix. A spin-diffusion bottleneck was postulated to explain the peculiar time evolution of ^{129}Xe signals in the clusters as well as the apparent discontinuity of ^{129}Xe polarization across the cluster boundaries. A self-contained *ab initio* model of nuclear spin diffusion in heterogeneous systems is developed here, incorporating the intrinsic T_1 relaxation towards the temperature-dependent equilibrium polarization and the spin-diffusion coefficients based on the measured NMR line widths and the known atomic densities in each compartment. This simple model provides the physical basis for the observed spin-diffusion bottleneck and is in a good quantitative agreement with the earlier measurements. A simultaneous fit of the model to the time-dependent NMR data at two different DNP frequencies provides excellent estimates of the cluster size, the intrinsic sample temperature, and ^{129}Xe T_1 constants. The model was also applied to the NMR data acquired during relaxation towards the thermal equilibrium after the microwaves were turned off, to estimate T_1 relaxation time constants inside and outside the clusters. Fitting the model to the data during and after DNP provides consistent estimates of the cluster size.

1. Introduction

Dynamic Nuclear Polarization (DNP) is a method used to dramatically enhance nuclear spin polarization by transferring spin alignment from the sparse unpaired electrons to the adjacent nuclei using resonant microwave irradiation [1]. Initial reports [2,3] on the DNP of ^{129}Xe raised expectations that this method of achieving nuclear hyperpolarizaion can compete with the more traditional optical pumping technology [4,5], especially in the context of high-volume noble-gas hyperpolarization for human-lung imaging [6,7]. However, the physics of nuclear spin interactions [8–10] in heterogeneous solid mixtures of a gaseous ingredient (such as xenon), a radical (such as commonly used trityl [11]) and a glassing agent (e.g. 1-propanol), necessary to prevent crystallization [12], is still not fully understood. As a result, recently reported polarization values for ^{129}Xe DNP [2,13] are still below 25% and lag significantly behind those in both optically-pumped xenon [5] and ^{13}C dissolution DNP [11].

Our recent low-temperature ^{129}Xe NMR measurements on solid xenon/1-propanol/trityl mixtures (3 mg (3.0 mol) Finland-acid radical, disslved in 97 mg (1.6 mmol) 1-propanol with 2.4 mmol of liquid xenon (natural abundance, 99.997% pure)) during DNP [13] present a remarkably simple experimentally-accessible physical system for studying DNP phenomena at the microscopic scale. Starting with a homogeneous low-temperature glassy matrix, containing both ^{129}Xe atoms and unpaired electrons, a simple warming up of the sample to ~125 K for several hours leads to spontaneous formation of pure xenon clusters embedded in xenon-depleted, but otherwise uniform, xenon/1-propanol/trityl host matrix, as shown in Fig. 1A. Volume-averaged polarization of xenon can be separately monitored in Xe clusters and in the glassy matrix, due to the very distinct local chemical shifts and NMR line widths of ^{129}Xe in each environment (Fig. 1B and C). Since DNP directly involves only the nuclear spins in the vicinity of unpaired electrons, more distant nuclei in the glassy matrix must be hyperpolarized by nuclear spin diffusion, a flip-flop nuclear magnetization transfer among stationary atoms [14]. Nuclear spin diffusion is also responsible for propagating DNP into pure-xenon clusters, where no free electrons are available.

We summarize our earlier corrected measurements [13] of the real-time volume-averaged ^{129}Xe polarization $\langle P(t)\rangle$ at two different DNP frequencies, ν^+ (filled circles) and ν^- (open circles) for pure-xenon clusters in Fig. 2. In the surrounding matrix, $\langle P(t)\rangle$ is well-described by a simple mono-exponential saturation towards

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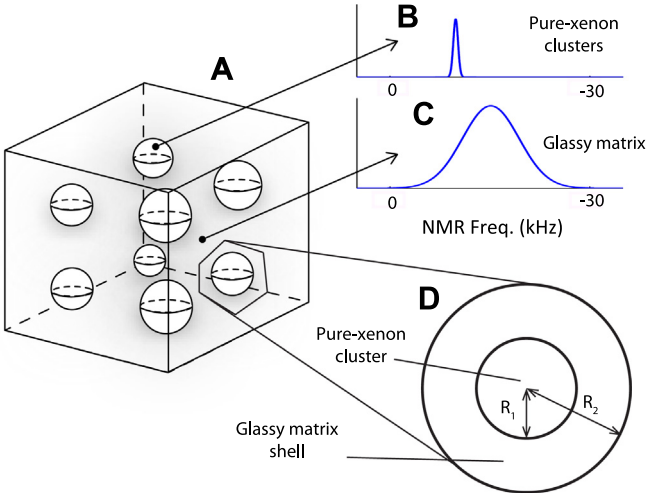

Fig. 1. (A) Sketch of pure-xenon clusters spontaneously formed in the glassy matrix of solid xenon/1-propanol/trityl mixture upon warming up to ~125 K. (B) The narrow peak in ^{129}Xe NMR spectra corresponds to pure xenon clusters. (C) The broad ^{129}Xe peak corresponds to solid xenon/1-propanol/trityl mixture. (D) Region of the glassy matrix containing the cluster is modeled by two concentric spheres of radii R_2 and R_1 respectively.

steady-state values $P_1^{\pm} \simeq \pm 4\%$ with the time constant of about an hour. The measurements begin at $t = 0$, when all ^{129}Xe polarization is destroyed by hard radio-frequency (rf) pulses. DNP at ν^- tends to populate the excited state of the nuclear Zeeman system, producing negative polarization (where we assign the positive sign to thermal-equilibrium polarization). At the early time points, the cores of the clusters are decoupled from the radical-rich matrix, and they polarize via a T_1 process towards their positive thermal equilibrium. At later times along the ν^- curve, negative DNP propagates across the cluster boundaries towards the cores, eventually resulting in the overall negative $\langle P(t)\rangle$ values. This peculiar crossover from positive to negative polarization during DNP at ν^-, highlighted in the insets Fig. 2D and E, along with an order-of-magnitude suppression of ^{129}Xe polarization in the clusters, was earlier explained by a hypothetical spin-diffusion bottleneck [13]. It was defined as a discontinuity in polarization across the cluster boundary that is proportional to the magnetization flux across it, analogous to the temperature drop across a thin styrofoam cup containing hot coffee. However, the physical basis of this postulated bottleneck was not derived quantitatively. Additionally, it was assumed that polarization outside the cluster is homogenous. As a result, the fit to the data included an empirical bottleneck constant, which was statistically coupled to the unknown cluster radius. Both parameters could only be estimated qualitatively, with error bars comparable to the estimated values.

Here we develop an *ab initio* analytical model of nuclear spin diffusion and T_1 spin relaxation in heterogeneous DNP mixtures. Our model assumes non-uniform local ^{129}Xe polarization $P(r, t)$ both in the clusters and in the glassy matrix, and incorporates spin-diffusion constants independently derived from the measured NMR line widths and the known atomic densities in each compartment. The discontinuity in *polarization gradient* across the cluster boundary is derived analytically by conserving the magnetization flux. The model reproduces the experimentally observed bottleneck behavior as a sharp but continuous drop of ^{129}Xe polarization across a thin layer of the glassy matrix surrounding the clusters. After eliminating the empirical bottleneck constant from our model, the fit to the experimental data yields a good quantitative estimate of the cluster size, while other fit parameters agree with the earlier empirical model. In this paper we also present the T_1 relaxation data acquired by switching off the microwave power immediately after obtaining the data of Fig. 2. Fitting our model, adapted to reproduce relaxation data, gives good estimates of the cluster size and the T_1 relaxation times inside and outside of the clusters when the microwave power is off. The model suggests significantly different T_1 estimates inside and outside the cluster, which is in agreement with observed data. Furthermore, the cluster sizes estimated by fitting the model to the DNP and the relaxation data sets are mutually consistent.

2. Analytical model

To model ^{129}Xe polarization, we assume spherical pure-xenon clusters of radius R_1, uniformly distributed in the surrounding xenon/1-propanol/trityl glassy matrix. The cluster-containing matrix regions are approximated by spherical shells (Fig. 1D), whose outer radius R_2 is calculated in Appendix A to be 1.49 R_1 from the known cluster-to-matrix volume ratio. Local ^{129}Xe polarization $P(r, t)$ at a distance $r = \sqrt{x^2 + y^2 + z^2}$ from the center of the cluster is modeled inside the cluster by combining the effects of spin-diffusion and those of T_1 relaxation:

$$\frac{\partial P(r,t)}{\partial t} = D_{s1}\nabla^2 P(r,t) + \frac{P_0 - P(r,t)}{T_1}, \quad 0 < r < R_1. \tag{1}$$

Outside the cluster, in the matrix region $R_1 < r < R_2$, an additional effect of DNP is taken into account:

$$\frac{\partial P(r,t)}{\partial t} = D_{s2}\nabla^2 P(r,t) + \frac{P_{DNP}^{\pm} - P(r,t)}{\tau_0}, \quad R_1 < r < R_2. \tag{2}$$

Here, $D_{s1} \approx 7.3 \times 10^{-14}$ cm^2/ s = 4.4 $\times 10^{-4}$ μm^2/min and $D_{s2} \approx 5.68 \times 10^{-6}$ μm^2/min are the ^{129}Xe nuclear spin-diffusion coefficients for natural-abundance pure xenon [15,16] and for the glass

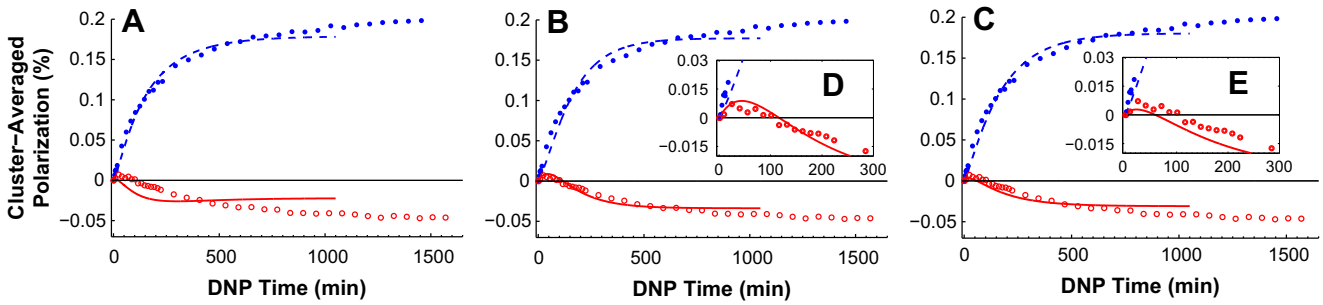

Fig. 2. Experimentally measured volume-averaged ^{129}Xe polarization in pure-xenon clusters as a function of time for positive and negative DNP (filled and open circles).* Simultaneous fitting of the model using the earlier simplest ((A), Eq. (9)),* earlier bottleneck ((B), Eq. (10)),* and the current *ab initio* ((C), Eqs. (6) and (8)) boundary conditions. Note the poor quality of the fit to the experimental data in (A). The insets (D) and (E) show a close-up view of the cluster-average polarization within minutes after initiating DNP. Note the peculiar behavior of polarization for $0 < t < 300$ min under negative DNP and the quality of the fit using the earlier bottleneck and the current *ab initio* boundary conditions. * Reproduced with permission from Ref. [13], after correcting the polarization values for small calibration coding errors discovered after publication.