

## SUPPLEMENTARY MATERIAL

### **Dynamic Nuclear Spin Polarization of Liquids and Gases in Contact with Nanostructured Diamond**

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## S1. Derivation of the master equation

We start by considering an isolated spin pair (see below) formed by an NV center ( $S=1$ ) and a nuclear spin ( $I=1/2$ ). We use the index  $i=1,2,\dots,6$  to respectively label the energy levels  $E_i$  corresponding to the set of eigenstates  $\{(m_S, m_I)\} = \left\{ \left(0, +\frac{1}{2}\right), \left(0, -\frac{1}{2}\right), \left(-1, +\frac{1}{2}\right), \left(-1, -\frac{1}{2}\right), \left(+1, +\frac{1}{2}\right), \left(+1, -\frac{1}{2}\right) \right\}$ , and write the detailed equilibrium equations

$$\frac{dN_i}{dt} = \sum_{j=1}^6 W_{ij}(N_j - N_i) + C_i, \quad (\text{S1})$$

where  $N_i$  represents the population (i.e., the fractional number of NV/nuclear spin pairs) in energy level  $i$ , and  $C_i$  is a constant.  $W_{ij}$  is the transition probability between energy levels  $i$  and  $j$  due to the dipolar interaction and is given by

$$W_{ij} = \left\langle \frac{1}{t\hbar^2} \left| \int_0^t \langle j | H_{dip}(t') | i \rangle e^{-i\omega_{ij}t'} dt' \right|^2 \right\rangle, \quad (\text{S2})$$

where  $\omega_{ij} = (E_j - E_i)/\hbar$ , and the outer brackets indicate ensemble average.  $H_{dip}(t)$  is the (time-dependent) dipolar Hamiltonian given by

$$H_{dip} = \frac{\mu_0}{4\pi} \frac{\gamma_S \gamma_I}{r^3} (\mathbf{I} \cdot \mathbf{S} - 3(\mathbf{S} \cdot \hat{\mathbf{r}})(\mathbf{I} \cdot \hat{\mathbf{r}})) \quad (\text{S3})$$

where  $\mathbf{r}$  is the vector separating spins  $S$  and  $I$  and  $\gamma_S, \gamma_I$  are the corresponding gyromagnetic ratios;  $\hbar$  denotes, as usual, Planck's constant divided by  $2\pi$ . To derive the Solomon equation governing the relaxation of nuclear spins in the presence of polarized NVs, we introduce the following definitions

$$\langle I \rangle \equiv \frac{1}{2}(N_1 - N_2 + N_3 - N_4 + N_5 - N_6);$$

$$\langle S_{0,-1} \rangle \equiv \frac{1}{2}(N_1 + N_2 - N_3 - N_4); \quad P_0 \equiv N_1 + N_2; \quad \langle I_0 \rangle \equiv \frac{1}{2}(N_1 - N_2);$$

$$\begin{aligned}
\langle S_{0,+1} \rangle &\equiv \frac{1}{2} (N_1 + N_2 - N_5 - N_6); & P_{-1} &\equiv N_3 + N_4; & \langle I_{-1} \rangle &\equiv \frac{1}{2} (N_3 - N_4); \\
\langle S_{-1,+1} \rangle &\equiv \frac{1}{2} (N_3 + N_4 - N_5 - N_6); & P_{+1} &\equiv N_5 + N_6; & \langle I_{+1} \rangle &\equiv \frac{1}{2} (N_5 - N_6).
\end{aligned}$$

Multiplying the even-indexed equations in (S1) by -1 and summing over all values of  $i$ , a lengthy calculation yields

$$\begin{aligned}
\frac{d\langle I \rangle}{dt} = & -\langle I \rangle \left( 2W_1(1 - P_0) + (W_2 + W_0)(1 - P_{+1}) + (\tilde{W}_2 + \tilde{W}_0)(1 - P_{-1}) \right) \\
& -\langle S_{0,-1} \rangle (W_2 - W_0) - \langle S_{0,+1} \rangle (\tilde{W}_0 - \tilde{W}_2) + C \quad (S4)
\end{aligned}$$

where  $C$  is a constant and we use the notation  $W_2 \equiv W_{14}$ ,  $W_0 \equiv W_{23}$ ,  $\tilde{W}_2 \equiv W_{25}$ ,  $\tilde{W}_0 \equiv W_{16}$ ,  $W_1 \equiv W_{34} = W_{56}$  as described in Fig. 1b. In calculating (S4) we use the identities  $W_{ij} = W_{ji}$ ,  $W_1^{(0)} \equiv W_{12} = 0$ , and  $\tilde{W}_3 \equiv W_{45} = 0 = W_{36} \equiv \tilde{W}_1'$ . We also assume that inter-nuclear couplings thermalize the nuclear spin bath so that  $\langle I_j \rangle = P_j \langle I \rangle$  for  $j=-1,0,+1$ . We find  $C$  by demanding that  $\frac{d\langle I \rangle}{dt}$  be zero at equilibrium (a condition we identify via the superindex  $e$ ); the Solomon equation then reads

$$\begin{aligned}
\frac{d\langle I \rangle}{dt} = & -(\langle I \rangle - I^{(e)}) \left( 2W_1(1 - P_0) + (W_2 + W_0)(1 - P_{+1}) + (\tilde{W}_2 + \tilde{W}_0)(1 - P_{-1}) \right) \\
& -(\langle S_{0,-1} \rangle - S_{0,-1}^{(e)}) (W_2 - W_0) - (\langle S_{0,+1} \rangle - S_{0,+1}^{(e)}) (\tilde{W}_0 - \tilde{W}_2) \quad (S5) \\
\cong & -\langle I \rangle \left( 2W_1(1 - P_0) + (W_2 + W_0)(1 - P_{+1}) + (\tilde{W}_2 + \tilde{W}_0)(1 - P_{-1}) \right) \\
& -\langle S_{0,-1} \rangle (W_2 - W_0) - \langle S_{0,+1} \rangle (\tilde{W}_0 - \tilde{W}_2),
\end{aligned}$$

where the last expression is valid in the limit of low magnetic fields ( $B < 500$  mT) considered here.

When the NV is continuously pumped into a given state  $m_S$ , the derivative in (S5) vanishes and the nuclear spin magnetization takes the stationary value  $\langle I \rangle_{m_S}$ . When  $m_S=0$ , we have  $P_0 =$

1,  $P_{+1} = P_{-1} = 0$  and  $\langle S_{0,-1} \rangle_0 = \langle S_{0,+1} \rangle_0 = 1/2$ ; the corresponding steady-state nuclear spin magnetization is then given by

$$\langle I \rangle_0 = -\frac{1}{2} \frac{(W_2 - W_0) - (\tilde{W}_2 - \tilde{W}_0)}{(W_2 + W_0 + \tilde{W}_2 + \tilde{W}_0)}. \quad (\text{S6})$$

By the same token, when  $m_S = -1$  we have  $P_{-1} = 1$ ,  $P_{+1} = P_0 = 0$ ,  $\langle S_{0,-1} \rangle_{-1} = -1/2$ ,  $\langle S_{0,+1} \rangle_{-1} = 0$ , and thus we obtain from (S5)

$$\langle I \rangle_{-1} = \frac{1}{2} \frac{(W_2 - W_0)}{(W_2 + 2W_1 + W_0)}. \quad (\text{S7})$$

Finally, when  $m_S = +1$ , then  $P_{+1} = 1$ ,  $P_{-1} = P_0 = 0$ ,  $\langle S_{0,+1} \rangle_{+1} = -1/2$ ,  $\langle S_{0,-1} \rangle_{+1} = 0$ , which yields

$$\langle I \rangle_{+1} = -\frac{1}{2} \frac{(\tilde{W}_2 - \tilde{W}_0)}{(\tilde{W}_2 + 2W_1 + \tilde{W}_0)}. \quad (\text{S8})$$

When the nuclear spin interacts with two NVs rather than just one as assumed above, the transition probabilities in Eq. (S2) simply take the form  $W_{i'j'} = \langle \frac{1}{t\hbar^2} \left| \int_0^t \langle j' | H_{dip}^{(1)}(t') + H_{dip}^{(2)}(t') | i' \rangle e^{-i\omega_{ij}t'} dt' \right|^2 \rangle$  where the subscripts 1,2 refer to each NV and  $|i'\rangle, |j'\rangle$  indicate the states of the three-particle system. These transition probabilities reduce to the sum of transition probabilities corresponding to each NV-nuclear spin pair plus a cross term of the form  $W_{i'j'}^{cross} = \langle \frac{2}{t\hbar^2} \left| \int_0^t \langle j' | H_{dip}^{(1)}(t') | i' \rangle e^{-i\omega_{ij}t'} dt' \right| \times \left| \int_0^t \langle j' | H_{dip}^{(2)}(t') | i' \rangle e^{-i\omega_{ij}t'} dt' \right| \rangle$ . It is simple to see that these cross terms are null except for the case where the NV states remain unchanged and the nuclear spin flips. Since Eq. (S6) does not depend on  $W_1$ , we conclude that the polarization dynamics upon direct optical illumination (in the absence of microwave) is less sensitive to NV ‘clustering’.

## S2. Derivation of the transition probabilities

Explicit expressions for the transitions probabilities can be obtained via Eqs. (S2) and (S3) by assuming that nuclear spins adsorbed on the diamond surface hop randomly from one position to the next with a correlation time  $\tau_c$ . Following Solomon's notation<sup>1</sup>, we first rewrite the dipolar interaction (Eq. (S3)) in the more convenient form

$$H_{dip}(t) = F_0(t) \left( I_z S_z - \frac{1}{4} (I_+ S_- + I_- S_+) \right) + F_1(t) (I_+ S_z + I_z S_+) + \\ + F_1^*(t) (I_- S_z + I_z S_-) + F_2(t) I_+ S_+ + F_2^*(t) I_- S_- , \quad (S9)$$

with

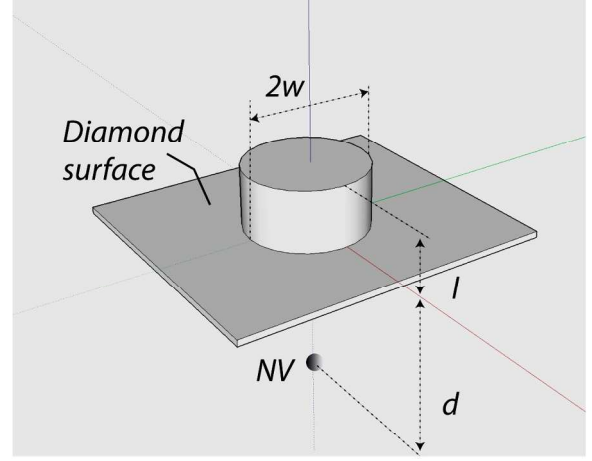
$$F_0(t) = \frac{k}{r^3} (1 - 3 \cos^2 \theta) ; \\ F_1(t) = -\frac{3}{2} \frac{k}{r^3} \sin \theta \cos \theta e^{i\varphi} ; \\ F_2(t) = -\frac{3}{4} \frac{k}{r^3} \sin^2 \theta e^{2i\varphi} . \quad (S10)$$

In the equations above the spherical coordinates  $(r, \theta, \varphi)$  of the interspin vector are assumed to be random functions of time, and  $k \equiv \mu_0 \gamma_I \gamma_S / 4\pi$ . Assuming, as usual, that  $\langle F_j(t) F_j^*(t + \tau) \rangle = \langle |F_j|^2 \rangle e^{-|\tau|/\tau_c}$  for  $j=0,1,2$  we find the transition probabilities

$$W_0 = \frac{\xi_0^{(NV)} \tau_c}{1 + \left( \left( \omega_{NV}^{(-1)} - \omega_I \right) \tau_c \right)^2} ; \quad \tilde{W}_0 = \frac{\xi_0^{(NV)} \tau_c}{1 + \left( \left( \omega_{NV}^{(+1)} - \omega_I \right) \tau_c \right)^2} ; \\ W_1 = \frac{\xi_1^{(NV)} \tau_c}{1 + \left( \omega_I \tau_c \right)^2} ; \\ W_2 = \frac{\xi_2^{(NV)} \tau_c}{1 + \left( \left( \omega_{NV}^{(-1)} + \omega_I \right) \tau_c \right)^2} ; \quad \tilde{W}_2 = \frac{\xi_2^{(NV)} \tau_c}{1 + \left( \left( \omega_{NV}^{(+1)} + \omega_I \right) \tau_c \right)^2} ; \quad (S11)$$

where  $\xi_0^{(NV)} = \hbar^2 \langle |F_0|^2 \rangle / 4$ ,  $\xi_1^{(NV)} = 2\hbar^2 \langle |F_1|^2 \rangle$ ,  $\xi_2^{(NV)} = 4\hbar^2 \langle |F_2|^2 \rangle$ ,  $\omega_{NV}^{(\pm 1)} = |\omega_{crys} \pm |\gamma_S|B|$ ,  $\omega_{crys} = 2\pi \times 2.87$  GHz, and  $\omega_I = \gamma_I B$ .

The exact value of  $\langle |F_j|^2 \rangle$  (and thus of  $\xi_j^{(NV)}$ ),  $j=0,1,2$ , depends on the geometry governing the interaction between the diamond-hosted NV and the nuclear spin adsorbed on the crystal surface. As an illustration we consider the surface topography in Fig. S1: An NV is a distance  $l+d$  below a cylindrical protrusion of diameter  $2w$  and height  $l$ . Assuming a diamond



**Fig. S1:** NV center a distance  $d$  below a cylindrical protrusion of radius  $w$  and height  $l$  on the diamond surface.

surface  $A$  characterized by a radius  $s_A \gg w$ , a direct calculation of  $\xi_0^{(NV)}$  yields

$$\begin{aligned} \xi_0^{(NV)} &= \frac{\hbar^2 k^2}{4A} \int_{Surf} da \frac{(1 - 3\cos^2\theta)^2}{r^6} \\ &= \frac{\pi \hbar^2 k^2}{2A} \left[ \frac{(f_0(u_m) - f_0(0))}{(d+l)^4} - \frac{f_0(u'_m)}{d^4} \right], \end{aligned} \quad (S12)$$

where

$$f_0(u) = -\frac{1}{4(1+u^2)^2} + \frac{1}{(1+u^2)^3} - \frac{9}{8(1+u^2)^4},$$

and  $u_m = w/(d+l)$ ,  $u'_m = w/d$ . By the same token, we obtain

$$\xi_1^{(NV)} = \frac{9\hbar^2 k^2}{2A} \int_{Surf} da \frac{\sin^2\theta \cos^2\theta}{r^6} = \frac{9\pi \hbar^2 k^2}{A} \left[ \frac{(f_1(u_m) - f_1(0))}{(d+l)^4} - \frac{f_1(u'_m)}{d^4} \right], \quad (S13)$$

$$\xi_2^{(NV)} = \frac{9\hbar^2 k^2}{4A} \int_{Surf} da \frac{\sin^4\theta}{r^6} = \frac{9\pi \hbar^2 k^2}{2A} \left[ \frac{(f_2(u_m) - f_2(0))}{(d+l)^4} - \frac{f_2(u'_m)}{d^4} \right], \quad (S14)$$

with

$$f_1(u) = -\frac{1}{6(1+u^2)^3} + \frac{1}{8(1+u^2)^4},$$

and

$$f_2(u) = -\frac{1}{4(1+u^2)^2} + \frac{1}{3(1+u^2)^3} - \frac{1}{8(1+u^2)^4}.$$

Combining (S12) and (S14) we get

$$\xi_2^{(NV)} - \xi_0^{(NV)} = \frac{\pi \hbar^2 k^2 w^2}{A} \left[ \frac{1}{(d^2 + w^2)^3} - \frac{1}{((d+l)^2 + w^2)^3} \right]. \quad (\text{S15})$$

An immediate consequence is that in the case of an NV beneath a flat surface ( $l=0$ ), we obtain

$$\left( \xi_2^{(NV)} - \xi_0^{(NV)} \right) \Big|_{(i)} = 0. \quad (\text{S16})$$

From Eq. (S16) we calculate

$$\left( \frac{W_2 - W_0}{W_2 + W_0} \right) \Big|_{(i)} = \frac{\omega_I}{\omega_{NV}^{(-1)}} \left( \frac{2 \left( \tau_c \omega_{NV}^{(-1)} \right)^2}{1 + \left( \omega_{NV}^{(-1)} \tau_c \right)^2} \right) \ll 1 \quad (\text{S17})$$

so long as  $\omega_{NV}^{(-1)} \gg \omega_I$  (the typical case in practice). Since, even for moderate fields  $\tilde{W}_j \ll W_j$ ,  $j=0, 2$ , we surmise from Eqs (S6)-(S8) that in the case of a flat surface the resulting nuclear polarization of surface spins must be low, a conclusion in agreement with the exact numerical calculations<sup>2</sup> of Fig. 2.

Next we consider the case of a cylindrical protrusion on the diamond surface where  $w \sim l$  and  $d=0$  (i.e., the NV sits at the center of its base, on the plane coincident with the rest of the diamond surface). Eq. (S15) then yields

$$\left( \xi_2^{(NV)} - \xi_0^{(NV)} \right) \Big|_{(ii)} \sim \frac{\pi \hbar^2 k^2}{A z^4}, \quad (\text{S18})$$

where  $z = w \sim l$  denotes the NV distance to the crystal surface. It is interesting to compare the above expression with that resulting from the opposite geometry, namely, the case where the NV sits below a pit of depth  $l = -d/2$ . Taking  $w \sim d/2$  we get

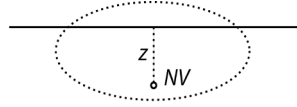
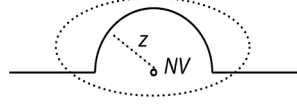
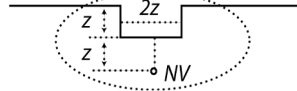
$$\left( \xi_2^{(NV)} - \xi_0^{(NV)} \right) \Big|_{(iii)} \approx -0.12 \frac{\pi \hbar^2 k^2}{A z^4}, \quad (\text{S19})$$

with  $z \sim w$  representing as before the distance to the surface. Thus, relative to the geometry in Eq. (S18), a pit on the crystal surface leads to a sign reversal and a significant reduction of the difference between the transition rate amplitudes. A summary for the different geometries including the case of a dome is presented in Table S1.

Finally, we consider the case of an inclined plane, i.e., the geometry where the direction normal to the surface forms an angle  $\theta_{NV}$  with the NV axis. As shown in Fig. S2, the angle  $\theta$  between the NV direction and the vector  $\mathbf{r} - \mathbf{r}_{NV} = (s \cos \phi, s \sin \phi, -z)$  connecting the NV center at  $\mathbf{r}_{NV} = (0, 0, -z)$  and the nuclear spin on the diamond surface is given by

$$\cos \theta = \frac{s \sin \phi \sin \theta_{NV} + z \cos \theta_{NV}}{(s^2 + z^2)^{1/2}}. \quad (\text{S20})$$

Combining (S20) with formulas (S12) and (S14), we find the generalized expressions for the transition rate constants

Geometry	$\xi_0/\chi$	$\xi_1/\chi$	$\xi_2/\chi$	
Flat surface	0.1875	0.3750	0.1875	
Cylindrical dome	0.5250	1.2000	3.5250	
Cylindrical pit	0.1682	0.1494	0.0203	

**Table S1:** Transition rate constants for different geometries. The constant  $\chi$  is given by  $\chi = \pi k^2 \hbar^2 \sigma / z^4$  and  $\sigma \equiv 1/A$  is the NV surface density



$$\xi_0^{(NV)}(\theta_{NV}) = \frac{3\chi}{32} \left[ 2 - 8 \sin^2 \theta_{NV} + \frac{3}{2} \sin^2 2\theta_{NV} + \frac{27}{4} \sin^4 \theta_{NV} \right], \quad (\text{S21})$$

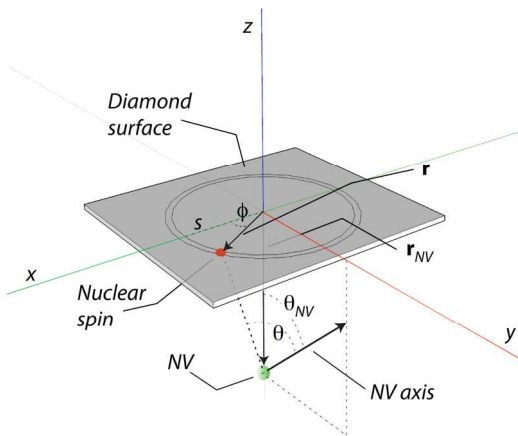
$$\xi_1^{(NV)}(\theta_{NV}) = \frac{9\chi}{32} \left[ \frac{4}{3} + 4 \sin^2 \theta_{NV} - \sin^2 2\theta_{NV} - \frac{9}{2} \sin^4 \theta_{NV} \right], \quad (\text{S22})$$

and

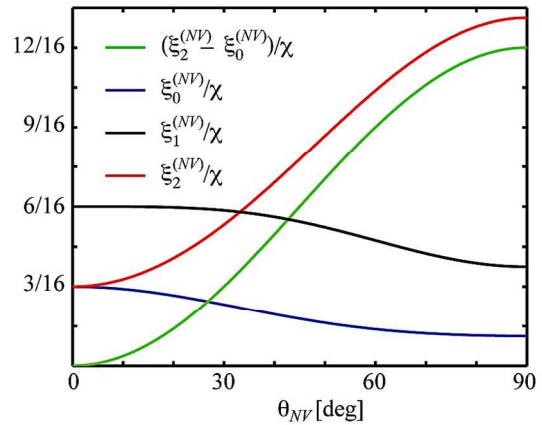
$$\xi_2^{(NV)}(\theta_{NV}) = \frac{3\chi}{32} \left[ 2 + \frac{3}{2} \sin^2 2\theta_{NV} + \frac{27}{4} \sin^4 \theta_{NV} \right], \quad (\text{S23})$$

where we define  $\chi \equiv \frac{\pi \hbar^2 k^2 \sigma}{z^4}$  and  $\sigma \equiv \frac{1}{A}$ . A plot of  $\xi_0^{(NV)}$ ,  $\xi_1^{(NV)}$ , and  $\xi_2^{(NV)}$  as a function of  $\theta_{NV}$  as calculated from formulas (S21)-(S23) is shown in Fig. S3. For  $\theta_{NV}=90$ , we find that  $(\xi_2^{(NV)} - \xi_0^{(NV)}) \Big|_{\theta_{NV}=90} \approx 2\chi/3 \sim 0.5 \times 10^8 \text{ s}^{-2}$  for NVs 3 nm below the surface. Comparison with, for example, the central plot in Fig. 3 of the main narrative shows that this value is much smaller than that obtained with a roughened surface.

It is worth emphasizing that the integrals involved in calculating  $\xi_j$  (Eqs. (S12)-(S14), (S21)-(S23)) result from taking ensemble average over all possible configurations between an NV center and a nuclear spin adsorbed on the diamond surface *at a given time*. The use of an



**Fig. S2:** Schematics of a shallow NV center whose axis forms an angle  $\theta_{NV}$  with the surface normal.



**Fig. S3:** Dependence of the transition rate constants  $\xi_0$ ,  $\xi_1$ , and  $\xi_2$  on the angle  $\theta_{NV}$  with the surface normal as calculated from formulas (S21)-(S23).

integral, therefore, does not reflect on assumptions regarding the detailed molecular trajectories on the surface. In particular, the present treatment remains valid even if molecules move from one position to the next via discrete jumps. This is because the condition of an exponentially-decaying time correlation function has no direct implications on how a molecule moves from one point in space to another (e.g., long-distance single hops versus short-distance multiple hops) or what the set of allowed positions is (e.g., discrete lattice versus a continuum). Correspondingly, our formulas are applicable to both liquids and gases, regardless the presumably different microscopic dynamics characterizing each case.

### S3. The influence of other nuclear spin relaxation channels

Assuming that  $1/T_{1I}^{(a)}$  is the nuclear spin relaxation rate due to mechanisms other than the interaction with NV centers, we rewrite Eq. (S5) in the form

$$\begin{aligned} \frac{d\langle I \rangle}{dt} \cong & -\langle I \rangle \left( 2W_1(1 - P_0) + (W_2 + W_0)(1 - P_{+1}) + (\tilde{W}_2 + \tilde{W}_0)(1 - P_{-1}) \right) \\ & - \frac{\langle I \rangle}{T_{1I}^{(a)}} - \langle S_{0,-1} \rangle (W_2 - W_0) - \langle S_{0,+1} \rangle (\tilde{W}_0 - \tilde{W}_2), \end{aligned} \quad (\text{S24})$$

where, as before, we assume negligible nuclear spin polarization in equilibrium. For NVs continuously pumped into  $m_S=0$ , the steady state nuclear magnetization is given by

$$\langle I \rangle_0 = -\frac{1}{2} \frac{\left( (W_2 - W_0) - (\tilde{W}_2 - \tilde{W}_0) \right)}{\left( W_2 + W_0 + \tilde{W}_2 + \tilde{W}_0 + \frac{1}{T_{1I}^{(a)}} \right)} = -\frac{1}{2} \lambda_0 \frac{\left( (W_2 - W_0) - (\tilde{W}_2 - \tilde{W}_0) \right)}{(W_2 + W_0 + \tilde{W}_2 + \tilde{W}_0)} \quad (\text{S25})$$

where  $\lambda_0 = 1/(1 + 1/\varepsilon_0)$  is called the ‘leakage factor’, and  $\varepsilon_0 = (W_2 + W_0 + \tilde{W}_2 + \tilde{W}_0)T_{1I}^{(a)}$  is the relative transition rate. Obviously, greater values of  $|\langle I \rangle_0|$  are obtained as  $\lambda_0$  approaches unity, which corresponds to larger values of  $\varepsilon_0$ . To gauge the influence of unpolarized spin-1/2

defects (such as P1 centers) on the nuclear spin pumping efficiency we write

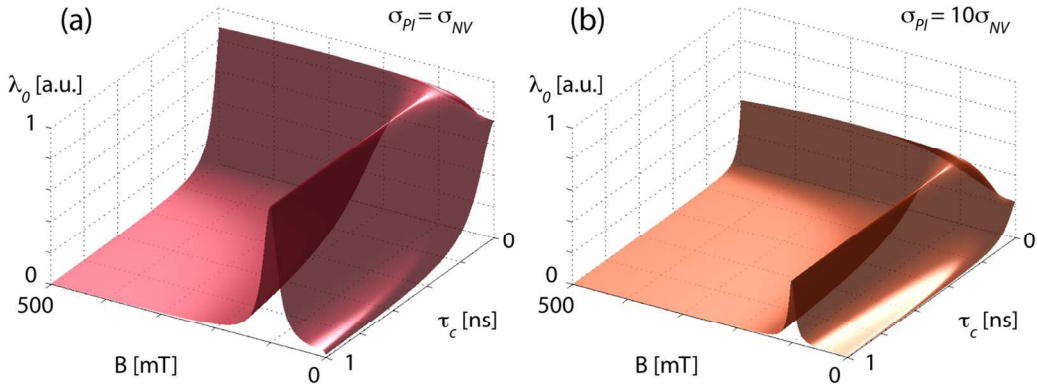
$$\frac{1}{T_{1I}^{(a)}} \sim \frac{1}{\hat{T}_{1I}^{(PI)}} = \left( W_2^{(PI)} + 2W_1^{(PI)} + W_0^{(PI)} \right) \quad (\text{S26})$$

where the expression for  $\frac{1}{\hat{T}_{1I}^{(PI)}}$  is that derived by Solomon for nuclear spins interacting with spin-1/2 paramagnetic centers<sup>1</sup>. For nuclear spins adsorbed on the diamond surface and interacting dipolarly with shallow paramagnetic impurities (PIs), a derivation similar to that presented in Section II yields the transition probabilities

$$W_0^{(PI)} = \frac{\xi_0^{(PI)} \tau_c}{1 + ((\omega_{PI} - \omega_I) \tau_c)^2} ; W_1^{(PI)} = \frac{\xi_1^{(PI)} \tau_c}{1 + (\omega_I \tau_c)^2} ; W_2^{(PI)} = \frac{\xi_2^{(PI)} \tau_c}{1 + ((\omega_{PI} + \omega_I) \tau_c)^2} ; \quad (\text{S27})$$

where  $\xi_0^{(PI)} = \hbar^2 \langle |F_0|^2 \rangle / 8$ ,  $\xi_1^{(PI)} = \hbar^2 \langle |F_1|^2 \rangle / 2$ ,  $\xi_2^{(NV)} = 2\hbar^2 \langle |F_2|^2 \rangle$ , and  $\omega_{PI} = \gamma_S B$ .

In Fig. S4a we plot the PI-induced leakage factor  $\lambda_0(B, \tau_c)$  for an NV optically pumped into  $m_S=0$  in the geometry of case (ii) (NV at the base of a dome) assuming that the NV and PI surface densities are identical. We find that nuclear spin relaxation is immune to paramagnetic impurities precisely where NV-induced DNP is most efficient. The leakage factor inevitably diminishes, though, as the concentration of PIs increases to values much larger than that of the



**Fig. S4:** (a) Leakage factor  $\lambda_0(B, \tau_c)$  due to spin-1/2 PIs for the case of NVs pumped onto  $m_S = 0$  assuming that both NVs and PIs act on nuclear spins from under a dome-like interface. The surface concentrations  $\sigma_{NV}$ ,  $\sigma_{PI}$  are the same. (b) Same as in (a) but for the case  $\sigma_{PI} = 10\sigma_{NV}$ .

NV (Fig. S4b).

#### S4. Calculating bulk nuclear spin polarization in the fluid

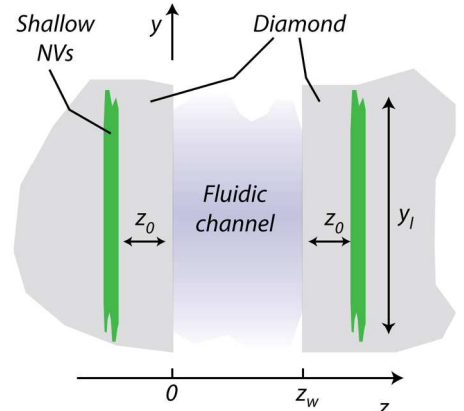
To account for molecular diffusion and flow throughout the microfluidic channel, we rewrite Eq. (S5) in the form

$$\begin{aligned} \frac{d\langle I \rangle(z, y, t)}{dt} = & -\langle I \rangle(z, y, t) \left( \frac{1}{\hat{T}_{1I}^{(NV)}(z, y)} + \frac{1}{T_{1I}^{(a)}(z, y)} + \frac{1}{T_{1I}^{(b)}} \right) - \frac{\langle S_0 \rangle}{T_{1I}^{(NV)}(z)} \\ & - \mathbf{v}(z) \cdot \nabla \langle I \rangle(z, y, t) + \nabla \cdot (D(z) \nabla \langle I \rangle(z, y, t)), \end{aligned} \quad (\text{S28})$$

where we neglect electron and nuclear spin equilibrium polarization and assume that the NVs are continuously pumped onto  $m_S = 0$  (i.e., the stationary NV polarization is approximately  $\langle S_{0,-1} \rangle_0 = \langle S_{0,+1} \rangle_0 \equiv \langle S_0 \rangle \approx 1/2$ ). In Eq. (S28) we define  $1/T_{1I}^{(NV)}(z, y) \equiv W^{(NV)}\kappa(z)\theta(|y| - y_l/2)$  and  $1/\hat{T}_{1I}^{(NV)}(z, y) \equiv \hat{W}^{(NV)}\kappa(z)\theta(|y| - y_l/2)$  where  $\theta(y)$  is the Heaviside function,  $y_l$  is the length of the implanted section of the the channel,  $\kappa(z) \equiv (z_0^4/(z_0 + z)^4 + z_0^4/(z_0 + z_w - z)^4)$  and  $z_0$  is the NV distance to the surface,  $z_w$  is the channel width, and  $z$  represents the position across the channel (in the  $[0, z_w]$  interval);  $W^{(NV)} \equiv ((W_2 - W_0) - (\tilde{W}_2 - \tilde{W}_0))|_{z_0}$  and  $\hat{W}^{(NV)} \equiv (W_2 + W_0 + \tilde{W}_2 + \tilde{W}_0)|_{z_0}$  calculated for NVs at a depth  $z_0$ . By the same token, we

write  $1/T_{1I}^{(a)}(z) \equiv W^{(PI)}\kappa(z)\theta(|y| - y_l/2)$  where  $W^{(PI)}$

represents the surface relaxation rate due to paramagnetic impurities other than the NV as discussed in Section S3. Finally,  $T_{1I}^{(b)}$  is the longitudinal relaxation time of nuclear spins within



**Fig. S5:** Schematics of the microfluidic geometry.

the fluid, and  $\mathbf{v}(z)$ ,  $D(z)$  respectively denote the fluid velocity and self-diffusion coefficient, in general, functions of the relative position across the microfluidic channel.

To get an estimate of the fluid nuclear spin polarization, we start by considering the simpler case where  $\mathbf{v} = 0$  and the fluid is confined to a channel-like volume of length  $y_l \gg z_w$ ; we also assume that the NV-implanted side walls — extending infinitely along the  $x$ -axis, perpendicular to the drawing in Fig. S5 — are homogeneously illuminated. Imposing, for simplicity, the condition  $D(z) = D$ , constant throughout the volume, and assuming that the channel width  $z_w$  is sufficiently small (e.g.,  $z_w \leq 1 \mu\text{m}$ ), we have for a fluid such as water  $T_{1I}^{(b)} \geq (W^{(NV)})^{-1} \sim (\hat{W}^{(NV)})^{-1} \gg \tau_w$ , where  $\tau_w = z_w^2/D$  is the molecular self-diffusion time across the channel (about  $100 \mu\text{s}$  for water in  $0.5\text{-}\mu\text{m}$ -wide channel). In this limit it follows that  $\langle I \rangle(z, y, t) \cong \langle \bar{I} \rangle(y, t)$ , i.e., the nuclear magnetization does not depend on the distance to the channel wall. On the other hand, and assuming that the length of the implanted region  $y_l$  is much longer than the diffusion length  $y_D = \sqrt{DT_{1I}^{(b)}}$ , molecules remain confined within the optically pumped region of the channel during the time required to reach a steady-state regime of dynamic polarization (of order  $T_{1I}^{(b)}$ ). In this latter case, nuclear spin order builds up uniformly throughout the illuminated region (i.e.,  $\langle I \rangle(y, t) = \langle I \rangle(t)$ ) and the dynamics can be modelled via the equation

$$\frac{d\langle I \rangle(t)}{dt} = -\langle I \rangle(t) \left( f(\hat{W}^{(NV)} + W^{(PI)}) + \frac{1}{T_{1I}^{(b)}} \right) - fW^{(NV)}\langle S_0 \rangle, \quad (\text{S29})$$

where the factor  $f \equiv \tau_a/(\tau_a + \tau_b) \cong \tau_a/\tau_b$  is the fractional time spent by molecules on the surface relative to that in the bulk of the fluid. In the stationary state (i.e., when  $\frac{d\langle I \rangle(t)}{dt} = 0$ ) we find the bulk nuclear spin polarization given by

$$\left(P_I^{(b)}\right)_{lim} = 2\langle I \rangle \cong -2fW^{(NV)}T_{1I}^{(b)}\langle S_0 \rangle, \quad (S30)$$

where we used that  $f \ll 1$  so that  $fT_{1I}^{(b)}(\widehat{W}^{(NV)} + W^{(PI)}) \ll 1$ . In thermal equilibrium we must have at the interface  $n_a/\tau_a = n_b/\tau_b$ , where  $n_a$  and  $n_b$  respectively denote the number of molecules adsorbed on the solid or in the bulk fluid; in the case of a 500-nm-wide channel we then get  $f = n_a/n_b \sim 2 \times 10^{-3}$ . Thus, for  $W^{(NV)} = 1 \text{ s}^{-1}$ ,  $T_{1I}^{(b)} = 10 \text{ s}$ , and  $\langle S_0 \rangle = 0.5$ , we obtain

$$\left(P_I^{(b)}\right)_{lim} \cong -2 \times 10^{-2}.$$

We note that for a fluid such as water (modelled in Fig. 5)  $y_D \sim 150 \mu\text{m}$ , which is comparable to (if not larger than) the length  $y_l$  one can reasonably expect to pump with a laser (at least in the absence of ancillary cavity-like structures). Therefore, part of the nuclear polarization ‘leaks’ outside of the illuminated region during the pumping process, which correspondingly leads to lower peak values of  $\left(P_I^{(b)}\right)_{lim}$ , as illustrated in Fig. 5a of the main text.

To tackle the more general case where  $y_l/y_D$  takes an arbitrary value, we return to Eq. (S28) and take the average across the channel under the assumption  $\langle I \rangle(z, y, t) \cong \langle \bar{I} \rangle(y, t) \equiv (1/z_w) \int_0^{z_w} \langle I \rangle(z, y, t) dz$  to get

$$\begin{aligned} \frac{d\langle \bar{I} \rangle}{dt}(y, t) = & -\langle \bar{I} \rangle(y, t) \left( f_{eff}(\widehat{W}^{(NV)} + W^{(PI)})\theta(|y| - y_l/2) + \frac{1}{T_{1I}^{(b)}} \right) \\ & -f_{eff}W^{(NV)}\theta(|y| - y_l/2)\langle S_0 \rangle - \frac{2v}{3} \frac{\partial \langle \bar{I} \rangle}{\partial y}(y, t) + D \frac{\partial^2 \langle \bar{I} \rangle}{\partial y^2}(y, t), \end{aligned} \quad (S31)$$

where we imposed a parabolic flow profile  $v_y(z) = v z(z_w - z)/z_w^2$ , dropped terms proportional to the gradient along  $z$ , and used the notation  $f_{eff} \equiv (1/z_w) \int_0^{z_w} \kappa(z) dz = \frac{z_0}{3z_w} (1 - z_0^3/(z_w + z_0)^3)$  to indicate the effective fraction of molecules experiencing a non-negligible coupling with the paramagnetic centers on the diamond surface. Note that with the

correspondence  $f_{eff} \leftrightarrow f$ , Eq. (S31) generalizes Eq. (S29) for arbitrary flow velocity  $v$  and implantation length  $y_l$ . The steady-state solution to Eq. (S31) in the absence of flow ( $v = 0$ ) is given by formula (6) of the main text.

### Supplementary References

<sup>1</sup> I. Solomon, “Relaxation processes in a system of two spins”, *Phys. Rev.* **99**, 559 (1955).

<sup>2</sup> Here we explicitly ignore level-anticrossing effects likely to take place in the immediate vicinity of 100 mT, where  $\omega_{NV}^{(-1)} \sim 0$ .