SUPPLEMENTAL MATERIAL

Superconducting STM tips in a magnetic field: geometry-controlled order of the phase transition

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In this Supplemental material we provide a microscopic description of superconductivity suppression in cone-shaped samples by a magnetic field. Starting with the Usadel equation and employing the adiabatic approximation for sharp tips, we derive an effective one-dimensional theory for superconductivity in the tip. By analyzing the quartic terms in the Ginzburg-Landau expansion we find that the quantum phase transition in a magnetic field is of the first order for sharp tips and second order for blunter tips. The procedure of numeric solution of the resulting equations is outlined.

I. EXPERIMENTAL DETAILS

Our measurements are carried out on an STM operating in ultrahigh vacuum (UHV) at a base temperature of 15 mK. External magnetic fields up to 14 T can be applied perpendicular to the sample surface and parallel to the tip axis [23]. The STM tips are mechanically cut *ex situ* under tension from polycrystalline V wire of 99.8% purity and then transferred to the STM. In the STM, the thin native oxide is removed by field emission on a V(100) sample, which was cleaned in several cycles of Ar ion sputtering and annealing to 1000°C. The tip apex is further optimized by short bias voltage pulses. Differential conductance (dI/dV) spectra are acquired at 15 mK by lock-in technique (modulation amplitude $\mathrm{V_{mod}} = 20\,\mu\mathrm{V}$, modulation frequency $\mathrm{f_{mod}} = 720\,\mathrm{Hz}$). The tunneling current is stabilized at $\mathrm{I_S} = 500\,\mathrm{pA}$ and $\mathrm{V_S} = 2.5\,\mathrm{mV}$.

II. GENERAL THEORETICAL FRAMEWORK

A. Sigma model and free energy

The most general approach to the description of dirty superconductors with spin polarization is based on the sigma-model technique [36]. In a unidirectional magnetic field (in the z direction), the action can be written as

$$S = S_+[Q_+] + S_-[Q_-] + \frac{\nu}{\lambda}\int d\mathbf{r}\,\mathrm{Tr}\,|\Delta|^2\,, \tag{S1}$$

where Q_+ and Q_- correspond spin-up and spin-down electrons described by the action

$$S_\sigma[Q] = \frac{\pi\nu}{8}\int d\mathbf{r}\,\mathrm{Tr}\Big\{D(\boldsymbol{\nabla} Q - i\mathbf{a}[\tau_3, Q])^2 - 4[(\epsilon - i\sigma h)\tau_3 + \hat{\Delta}]Q\Big\}. \tag{S2}$$

Here $\mathbf{a} = e\mathbf{A}/c$, $\mathbf{A}$ is the vector potential for the magnetic field $\mathbf{B}$, $h = g\mu_B B/2$ is the Zeeman energy, ν is the density of states at the Fermi energy per one spin projection, and $\lambda = \ln(2\omega_D/\Delta_0)$ is the Cooper-channel interaction constant (with the zero-temperature bulk gap Δ_0, and the Debye energy ω_D). The field $Q(\mathbf{r})$ is a matrix in the tensor product of the Nambu space, the replica space and the Matsubara-energy space, with trace in Eq. (S2) acting in all these spaces. The matrix Q satisfies $Q^2 = 1$.

We work in the units $\hbar = 1$ and $k_B = 1$ and restore them in the final expressions.

In what follows we restrict ourselves with the stationary replica-symmetric saddle-point solutions which allows to discard the replica space and consider only diagonal-in-energy field Q with the standard angular parametrization

$$Q(\epsilon, \mathbf{r}) = \begin{pmatrix} \cos\theta & e^{i\phi}\sin\theta \\ e^{-i\phi}\sin\theta & -\cos\theta \end{pmatrix}, \tag{S3}$$

where $\theta_\epsilon(\mathbf{r})$ and $\phi_\epsilon(\mathbf{r})$ depend on $\mathbf{r}$ and the Matsubara energy $\epsilon = \pi T(2n+1)$. At the same time, the matrix $\hat{\Delta}$ becomes replica-symmetric and time-independent:

$$\hat{\Delta} = \begin{pmatrix} 0 & \Delta e^{i\varphi} \\ \Delta e^{-i\varphi} & 0 \end{pmatrix} = \Delta(\tau_1\cos\varphi - \tau_2\sin\varphi). \tag{S4}$$

The free energy $F = TS$ can be written in terms of the spin-up component $Q = Q_+$ (the spin-down component is accounted for by taking the real part) as

$$F = \frac{\pi\nu}{2}T\sum_\epsilon \int d\mathbf{r}\,\mathrm{Re}\Big\{D[(\nabla\theta)^2 + \sin^2\theta(\nabla\phi - 2\mathbf{a})^2] - 4(\epsilon - ih)\cos\theta - 4\Delta\cos(\phi - \varphi)\sin\theta\Big\} + \frac{\nu}{\lambda}\int \Delta^2 d\mathbf{r}. \tag{S5}$$

B. Usadel equations

Varying the free energy (S5) with respect to the spectral angles θ and ϕ we get the system of Usadel equations:

$$\frac{D}{2}[-\nabla^2\theta + \sin\theta\cos\theta(\nabla\phi - 2\mathbf{a})^2] + (\epsilon - ih)\sin\theta - \Delta\cos(\phi - \varphi)\cos\theta = 0, \tag{S6}$$

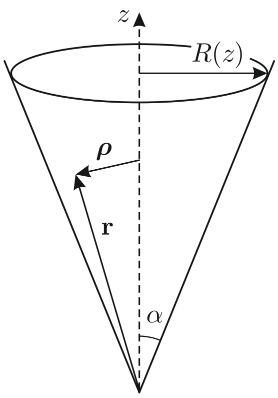

FIG. S1: An axially-symmetric STM tip with the surface specified by the function $R(z)$. Sharp conical tips correspond to $R(z) \approx \alpha z$ with $\alpha \ll 1$.

$$-\frac{D}{2}\nabla(\sin^2\theta(\nabla\phi - 2\mathbf{a})) + \Delta\sin(\phi-\varphi)\sin\theta = 0. \quad \text{(S7)}$$

The order parameter is to be determined from the self-consistency equation

$$\Delta(\mathbf{r})e^{i\varphi(\mathbf{r})} = \lambda\, 2\pi T \sum_{\epsilon>0} \operatorname{Re}\sin\theta_\epsilon(\mathbf{r})e^{i\phi_\epsilon(\mathbf{r})}. \quad \text{(S8)}$$

C. Adiabatic approximation for sharp tips

Magnetic field penetrating into a bulk superconductor generates vortices. The vortex core is characterized by the 2π phase winding and a normal core of size ξ. For a sharp tip in a magnetic field $B > B_{c,\text{bulk}}$, it happens that superconductivity may not be completely destroyed but survives in a small region near the apex, with the relevant tip cross-section $\pi R^2(z)$ smaller than ξ^2. In this case no vortex is formed and one can search for the localized solution with $\varphi = \phi = 0$. For an axially symmetric tip we choose the Landau gauge, $\mathbf{A} = [\mathbf{B}, \mathbf{r}]/2$. Then the solution $\theta(z,\rho)$ becomes a function of z and the distance $\rho = \sqrt{x^2+y^2}$ from the tip axis (see Fig. S1).

Thus we get a single nonlinear equation for the function $\theta_\epsilon(z,\rho)$:

$$\frac{D}{2}[-\nabla^2\theta + H^2\rho^2\sin\theta\cos\theta] + (\epsilon - ih)\sin\theta - \Delta\cos\theta = 0, \quad \text{(S9)}$$

where we defined $H = eB/c$. The self-consistency equation (S8) takes the form:

$$\Delta(\mathbf{r}) = \lambda\, 2\pi T \sum_{\epsilon>0} \operatorname{Re}\sin\theta_\epsilon(\mathbf{r}). \quad \text{(S10)}$$

Equations (S9) and (S10) should be supplemented by the boundary condition of vanishing supercurrent component normal to the tip surface. In the Landau gauge with $\varphi = \phi = 0$ this condition is met automatically.

In general, the system (S9), (S10) can be solved only numerically. Analytical treatment is possible for a sharp-tip geometry where one can employ an adiabatic approximation. In this approximation, we assume that the ρ dependence of $\theta_\epsilon(z,\rho)$ and $\Delta(z,\rho)$ can be neglected. This is justified provided that $R(L) \ll \xi$, where L is the typical size of the localized solution in the z direction [for a conical geometry, see Eq. (S30)].

Under such an approximation, the free energy difference between the superconducting and normal states can be written as a functional of $\theta(z)$ and $\Delta(z)$:

$$F_S - F_N = \frac{\pi\nu}{2} T \sum_\epsilon \int \operatorname{Re}\Big[D\left(\theta'^2 + \frac{1}{2}H^2R^2(z)\sin^2\theta\right) + 4(\epsilon - ih)(1-\cos\theta) - 4\Delta\sin\theta\Big]\pi R^2(z)\,dz + \frac{\nu}{\lambda}\int \Delta^2 \pi R^2(z)\,dz. \quad \text{(S11)}$$

The factor 1/2 in the first line stems from the averaging over the cross section:

$$\int d\mathbf{r}\,\rho^2 = \int dz \int_0^{R(z)} 2\pi\rho^3 d\rho = \frac{1}{2}\int \pi R^4(z)\,dz.$$

Taking the derivatives of the free energy (S11) with respect to $\theta_\epsilon(z)$ we arrive at the effective one-dimensional Usadel equation in the adiabatic approximation:

$$\frac{D}{2}\left[-\theta_\epsilon'' - \frac{2R'(z)}{R(z)}\theta_\epsilon' + \frac{1}{4}H^2R^2(z)\sin 2\theta_\epsilon\right] + (\epsilon - ih)\sin\theta_\epsilon = \Delta(z)\cos\theta_\epsilon. \quad \text{(S12)}$$

The $T=0$ self-consistency equation takes the form

$$\frac{\Delta(z)}{\lambda} = \operatorname{Re}\int_0^{\omega_D} \sin\theta_\epsilon(z)\,d\epsilon. \quad \text{(S13)}$$

Solution of Eqs. (S12) and (S13) should be substituted to Eq. (S11) in order to determine the free energy of the superconducting state.

III. INSTABILITY OF THE NORMAL STATE

In this section, we find the point of the superconducting transition at $T=0$, *assuming* that the transition is of the second order. To this end, we expand Eqs. (S12) and (S13) and find a point where appearance of a finite Δ and θ_ϵ becomes costless.

The spacial profile of $\theta(z)$ is determined by the spectrum of the linearized operator in Eq. (S12):

$$\frac{D}{2}\left[-\frac{\partial^2}{\partial z^2} - \frac{2R'(z)}{R(z)}\frac{\partial}{\partial z} + \frac{H^2R^2(z)}{2}\right]\psi_n(z) = E_n\psi_n(z). \quad \text{(S14)}$$

The second-order instability corresponds to the lowest eigenvalue, E_0. Assuming that both $\theta_\epsilon(z)$ and $\Delta(z)$ are proportional to $\psi_0(z)$ we get

$$\frac{1}{\lambda}\Delta = \mathrm{Re}\int_0^{\omega_D} \theta\, d\epsilon, \tag{S15}$$

$$E_0\theta + (\epsilon - ih)\,\theta = \Delta. \tag{S16}$$

Hence,

$$\frac{1}{\lambda}\Delta = \Delta\,\mathrm{Re}\int_0^{\omega_D} \frac{d\epsilon}{E_0+\epsilon-ih} = \Delta \ln\frac{\omega_D}{\sqrt{E_0^2+h^2}}. \tag{S17}$$

Expressing λ via the $T=0$ value of the gap in a bulk superconductor Δ_0, we get for the instability point:

$$E_0^2(H) + h^2 = \left(\frac{\Delta_0}{2}\right)^2. \tag{S18}$$

Our result (S18) formally coincides with the zero-dimensional result of Ref. 25, with the tip geometry entering only through E_0. Note that according to Eq. (S14), $E_0(H)$ is a function of the orbital magnetic field.

IV. ORDER OF THE TRANSITION

Here, we derive the quartic term in the Ginzburg-Landau expansion of the free energy in powers of Δ. The sign of this term determines the order of the phase transition.

A. General case

Assuming that

$$\Delta(z) = C\psi_0(z), \tag{S19}$$

we solve the Usadel equation (S12) keeping the next-to-leading term:

$$\theta(z) = \theta_1(z) + \theta_3(z). \tag{S20}$$

Choosing $\psi_0(z)$ to be normalized, $\langle\psi_0^2\rangle = 1$, we get

$$\theta_1(z) = \frac{C}{E_0+\epsilon-ih}\psi_0(z) \tag{S21}$$

and

$$\theta_3(z) = \left(\frac{A}{(E_0+\epsilon-ih)^3} + \frac{B+(\epsilon-ih)F}{(E_0+\epsilon-ih)^4}\right)\psi_0(z), \tag{S22}$$

where

$$A = -\frac{\langle\psi_0^4\rangle}{2}, \quad B = \frac{DH^2}{6}\langle\psi_0^4R^2\rangle, \quad F = \frac{\langle\psi_0^4\rangle}{6}, \tag{S23}$$

and angular brackets stand for the averaging over the volume of the tip:

$$\langle\ldots\rangle = \int \ldots \pi R^2(z)\, dz. \tag{S24}$$

Substituting (S20) back into Eq. (S11), after some algebra we get the main result for the free energy:

$$\begin{aligned} F_S - F_N &= \nu\ln\frac{\sqrt{E_0^2+h^2}}{\Delta_0/2}C^2 \\ &+ \frac{\nu}{4\,(E_0^2+h^2)^3}\left[\frac{E_0^3-3h^2E_0}{18}\left(E_0\langle\psi_0^4\rangle - DH^2\langle\psi_0^4R^2\rangle\right)\right. \\ &\left.+\frac{E_0^4-h^4}{2}\langle\psi_0^4\rangle\right]C^4 + \ldots \end{aligned} \tag{S25}$$

B. 0D case

In the 0D geometry, $\psi_0 = 1/\sqrt{V}$ is a constant, and the lowest eigenvalue is given by

$$E_0(H) = DH^2\langle R^2\rangle/4V \propto H^2. \tag{S26}$$

The free energy difference reads:

$$\begin{aligned} F_S - F_N &= \nu\ln\frac{\sqrt{E_0^2+h^2}}{\Delta_0/2}C^2 \\ &+ \frac{\nu E_0^4}{24V\,(E_0^2+h^2)^3}\left[1+6\left(\frac{h}{E_0}\right)^2 - 3\left(\frac{h}{E_0}\right)^4\right]C^4. \end{aligned} \tag{S27}$$

The phase transition is of the second order as long as

$$\frac{h}{E_0(H_c)} < \sqrt{1+\frac{2\sqrt{3}}{3}} = 1.47\ldots, \tag{S28}$$

which coincides with the result of Maki [25] for thin films in a parallel magnetic field.

The transition is of the second order for large magnetic fields, $B > B^*$, where in dimensional units

$$B^* = \frac{3g}{\pi}\frac{m_*/m}{k_F l}\frac{\Phi_0 V}{\langle R^2\rangle}, \tag{S29}$$

with $\Phi_0 = \pi\hbar c/e$ being the superconducting flux quantum. The ratio of the effective electron mass m_* to the bare mass m originates from the ratio μ_B/D since $D = v_F l/3 = \hbar k_F l m/3m_*$.

C. Conical tip

For a sharp conical tip, $R(z) = \alpha z$ with $\alpha \ll 1$, Eq. (S14) becomes the Schrödinger equation for the 3D oscillator. Its normalized ground state wave function decaying at the scale $L \sim 1/\sqrt{H\alpha}$ has the form

$$\psi_0(z) = \frac{2^{5/8} H^{3/4}}{\pi^{3/4} \alpha^{1/4}} \exp\left(-\frac{H\alpha z^2}{2\sqrt{2}}\right), \tag{S30}$$

and the ground-state energy is given by

$$E_0(H) = \frac{3\alpha H D}{2\sqrt{2}}. \tag{S31}$$

Note that for a conical tip, $E_0(H) \propto H$, contrary to the 0D case [Eq. (S26)]. As a result, the ratio h/E_0 does not depend on the magnetic field and can be represented in the form:

$$\frac{h}{E_0} = \frac{\alpha_c}{\alpha}, \tag{S32}$$

where we introduced the critical angle α_c defined as

$$\alpha_c = \frac{g}{\sqrt{2}} \frac{m_*/m}{k_F l}, \tag{S33}$$

where the origin of the ratio m_*/m has been discussed above.

Substituting (S30) into (S25), we get

$$F_S - F_N = \nu \ln \frac{\sqrt{E_0^2 + h^2}}{\Delta_0/2} C^2 + \frac{\nu H^{3/2}(E_0^2 - h^2)}{8 \cdot 2^{1/4} \pi^{3/4} \alpha^{1/2}} C^4. \tag{S34}$$

The quadratic term determines the absolute instability of the normal state, which takes place at the field [in accordance with Eq. (S18)]

$$B_{\text{inst}} = \frac{B_p}{\sqrt{2}} \frac{1}{\sqrt{1 + (\alpha/\alpha_c)^2}}, \tag{S35}$$

where $B_p = \sqrt{2}\Delta_0/g\mu_B$ is the paramagnetic limit (realized in thin cylinders, where $\alpha \to 0$), when superconductivity is destroyed by breaking a Cooper pair due to the Zeeman splitting.

At the critical field, $B \sim B_{\text{inst}}$, the tip radius at the length L can be estimated as

$$R^2(L)/\xi^2 \sim \alpha\sqrt{\alpha^2 + \alpha_c^2} \ll 1, \tag{S36}$$

which justifies the adiabatic approximation employed.

Analysis of the quartic term in Eq. (S34) demonstrates that the magnetic field B_{inst} marks a real second-order quantum phase transition ($B_c = B_{\text{inst}}$) provided $\alpha > \alpha_c$ (when the spin effect of the magnetic field is less important than its orbital effect). For sharper tips with $\alpha < \alpha_c$ (the leading Zeeman term), the first-order transition occurs at lower fields $B_c < B_{\text{inst}}$. In the latter case, the Ginzburg-Landau expansion (S34) is no longer valid and one has to solve the full nonlinear 1D system (S12) and (S13) [or even the 2D system (S9) and (S10), if the tip is sufficiently blunt such that the adiabatic approximation cannot be applied].

V. NUMERICAL SOLUTION FOR CONICAL TIPS

In dimensional units, the system (S12) and (S13) for the conical tip with a small opening angle α can be written in the form (we set $g = 2$ for vanadium):

$$\frac{\hbar D}{2}\left[-\theta_\epsilon'' - \frac{2}{z}\theta_\epsilon' + \left(\frac{\pi B\alpha}{2\Phi_0}\right)^2 z^2 \sin 2\theta_\epsilon\right] + (\epsilon - i\mu_B B)\sin\theta_\epsilon = \Delta(z)\cos\theta_\epsilon, \tag{S37}$$

$$\frac{\Delta(z)}{\lambda} = \operatorname{Re}\int_0^{\hbar\omega_D} \sin\theta_\epsilon(z)\, d\epsilon. \tag{S38}$$

The free energy difference is given by

$$F_S - F_N = \pi\nu \int_0^{\hbar\omega_D} \frac{d\epsilon}{2\pi} \int \operatorname{Re}\Bigg[\hbar D\left(\theta_\epsilon'^2 + \frac{1}{2}\left(\frac{\pi B\alpha}{\Phi_0}\right)^2 z^2 \sin^2\theta_\epsilon\right) + 4(\epsilon - i\mu_B B)(1 - \cos\theta_\epsilon) - 4\Delta(z)\sin\theta_\epsilon\Bigg]\pi\alpha^2 z^2\, dz + \frac{\nu}{\lambda}\int \Delta^2(z)\pi\alpha^2 z^2\, dz. \tag{S39}$$

In terms of the dimensionless z-coordinate

$$\tilde{z} = \sqrt{\frac{\pi B\alpha}{2\Phi_0}}\, z, \tag{S40}$$

these equations acquire the form of Eqs. (3) and (5):

$$\frac{\alpha/\alpha_c}{3\sqrt{2}}\mu_B B\left(-\theta_\epsilon'' - \frac{2}{\tilde{z}}\theta_\epsilon' + \tilde{z}^2 \sin 2\theta_\epsilon\right) + (\epsilon - i\mu_B B)\sin\theta_\epsilon = \Delta(\tilde{z})\cos\theta_\epsilon, \tag{S41}$$

$$\frac{\Delta(\tilde{z})}{\lambda} = \mathrm{Re}\int_0^{\hbar\omega_D} \sin\theta_\epsilon(\tilde{z})\, d\epsilon. \tag{S42}$$

The free energy difference is given by

$$F_S - F_N = \pi\nu\alpha^2\left(\frac{2\Phi_0}{\pi B\alpha}\right)^{3/2}\Delta\mathcal{F}, \tag{S43}$$

where

$$\Delta\mathcal{F} = \int_0^\infty \tilde{z}^2\, d\tilde{z}\left\{\frac{\Delta^2(\tilde{z})}{\lambda} + \int_0^{\hbar\omega_D} d\epsilon\, \mathrm{Re}\left[\frac{\alpha/\alpha_c}{3\sqrt{2}}\mu_B B\left(\theta_\epsilon'^2 + 2\tilde{z}^2\sin^2\theta_\epsilon\right) + 4(\epsilon - i\mu_B B)(1-\cos\theta_\epsilon) - 4\Delta(\tilde{z})\sin\theta_\epsilon\right]\right\}. \tag{S44}$$

Equations (S41) and (S42) are used to numerically calculate the magnetic field dependence of $\Delta(\tilde{z})$ for superconducting cones with $0.2 \leq \alpha/\alpha_c \leq 4$. This is done iteratively by starting with some $\Delta(\tilde{z})$, solving numerically the differential Usadel equation (S41), and then obtaining a new profile of $\Delta(\tilde{z})$ from the self-consistency equation (S42). The calculations are performed in `MATLAB` using the `bvp5c` solver. As initial starting configuration, the superconducting order parameter in the tip is chosen to decay as a Gaussian function of the dimensionless coordinate $\tilde{z}$ [cf. Eq. (S30)]:

$$\Delta(\tilde{z}) = \Delta(0)\, e^{-\tilde{z}^2}. \tag{S45}$$

The solution provided by `bvp5c` obeys the boundary conditions $\phi'(0) = 0$ and $\phi(z \to \infty) = 0$. The iterative procedure is repeated until the difference between the solutions of the last two iterations (n and $n-1$) lies below a given threshold value t:

$$\sum_{\tilde{z}} \left(\Delta_n(\tilde{z}) - \Delta_{n-1}(\tilde{z})\right)^2 < t. \tag{S46}$$

On the one hand, the threshold value should be as small as possible to achieve a converging solution. On the other hand, small thresholds t drastically increase the number of iterations resulting in unmanageable computation times. The analytical expression for the critical field (S35) is used to identify a suitable threshold value, which offers acceptable accuracy in combination with manageable computational times. According to the analytic expression, the superconducting gap should vanish for $B > B_{\mathrm{inst}}$ [Eq. (S35)] and, therefore, the precision of the analytic calculations is increased until the numerical error of the superconducting gap at the critical field is below three percent of its initial value: $\Delta(B_c) < 0.03\Delta(0)$. The calculated Usadel spectra were further analyzed in terms of the EMM (see Fig. 3). For the fits, we use $b = 0$, since the effect of spin-orbit coupling is small, and $\zeta = 0$, since orbital depairing effects are already taken care of by the broadening parameter Γ.

VI. ORBITAL DEPAIRING

The magnetic field dependence of the experimentally measured DOS in V tips is analyzed by a fitting routine based on the EMM. In Fig. S2, the orbital depairing parameter ζ is shown as function of the magnetic field. The effect of ζ is minor in comparison with the overall broadening by Γ discussed before. The orbital depairing is a measure of the kinetic energy of Cooper pairs and is expected to increase in magnetic fields as $\zeta \propto B^2$ [25]. The depairing parameter ζ extracted for the superconducting V tips reveals a monotonic magnetic field dependence. However, the rate of increase strongly depends on the tip indicating the influence of the detailed tip geometry. In general, larger values of ζ are found for V tips with more broadened dI/dV spectra. We note that (unlike Γ) ζ does not fill the SC gap.

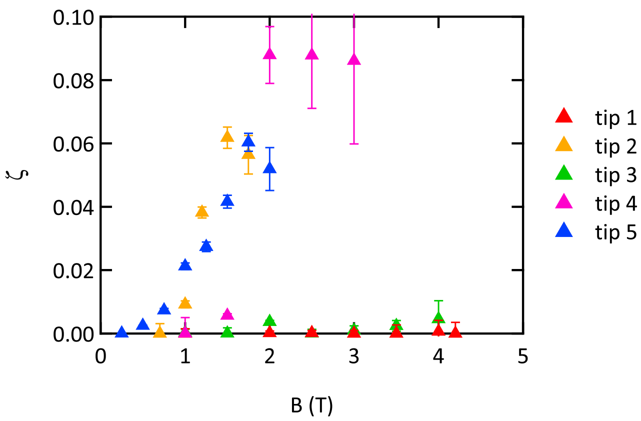

FIG. S2: Magnetic field dependence of the depairing parameter ζ for the V tips. The parameter ζ increases with increasing magnetic field. Its initial value as well as the rate of change depend on the tip indicating the geometrical influence.