On the superparamagnetic size limit of nanoparticles on a ferroelectric substrate

A Sukhov\textsuperscript{1}, L Chotorlishvili\textsuperscript{1}, P P Horley\textsuperscript{2}, C-L Jia\textsuperscript{3}, S K Mishra\textsuperscript{4} and J Berakdar\textsuperscript{1}

\textsuperscript{1} Institut für Physik, Martin-Luther Universität Halle-Wittenberg, 06120 Halle (Saale), Germany
\textsuperscript{2} Centro de Investigación en Materiales Avanzados (CIMAV S.C.), Chihuahua/Monterrey, 31109 Chihuahua, Mexico
\textsuperscript{3} Key Laboratory for Magnetism and Magnetic Materials of the MOE, Lanzhou University, Lanzhou 730000, People’s Republic of China
\textsuperscript{4} Department of Applied Physics, Indian Institute of Technology, Banaras Hindu University, Varanasi-221005, India

E-mail: alexander.sukhov@physik.uni-halle.de

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Abstract

When decreasing the size of nanoscale magnetic particles, their magnetization becomes vulnerable to thermal fluctuations as the superparamagnetic limit approaches, thus hindering applications relying on a stable magnetization. Here, we theoretically investigate how a magnetoelectric coupling to a ferroelectric substrate modifies the superparamagnetic limit, with a special focus on the possible realization of substantially smaller multiferroic clusters with thermally stable magnetization. For an estimate of cluster size we perform calculations for iron nanoparticles multiferroically coupled to a BaTiO\textsubscript{3} substrate. Our numerical results indicate that steering the polarization of BaTiO\textsubscript{3} with electric fields affects the magnetism of the deposited magnetic clusters. The work provides a suggestion on how the strength of the magnetoelectric coupling might be extracted from telegraph noise experiments.

Keywords: superparamagnetic limit, multiferroics, nanoparticles

1. Introduction

Fuelled by novel fabrication, miniaturization and characterization techniques, nanomagnetism has been a crucial element in the ongoing advances in nanotechnology; for example, the current high-density information magnetic storage is achieved by nanostructures having out-of-plane (or perpendicular) magnetization [1]. Further decreasing the size of the nanostructures would allow for yet higher storage capacity, but at some critical size (depending on the material, typically below 3–50 nm) the magnetization starts to randomly flip its direction due to thermal activation, which marks the superparamagnetic state of the system [2]. This phenomenon is well known, with implications for a variety of applications including magnetic nanoparticles or fluids, magnetic refrigeration, magnetic resonance imaging and drug delivery schemes [3–6]. Thus, finding ways to tune superparamagnetism and/or to stabilize the magnetization while downsizing the nanoclusters is an issue of key importance. A highly desirable way would be to achieve this goal via external electric means, which would imply less energy consumption than magnetic fields and more flexibility than the synthesis of new material compositions with engineered magnetic anisotropy energy density $K$, which is a decisive factor for superparamagnetism. Indeed, the Néel relaxation time $\tau_N$, i.e. the mean time between successive flips, depends exponentially on the magnetic anisotropy energy $K V$ ($V$ is the particle volume) with respect to the thermal energy $k_B T$ (i.e. $\tau_N = \tau_0 \exp(\frac{K V}{k_B T})$), where $\tau_0$ is a material specific attempt time). Small variations in the energy barrier $K V$ substantially affect $\tau_N$. Hence, roughly speaking, increasing $K$ allows for smaller $V$ while maintaining $\tau_N$. From this perspective, coupled ferroelectric (FE)/ferromagnetic (FM) nanostructures [7–10] such as those schematically displayed in figure 1 or when FM nanoparticles are embedded into FE [11] or multiferroic [12] matrices, are highly interesting.
On the other hand, the dynamics are more elaborate, since an evolution of the polarization-affected magnetization triggers polarization dynamics that in turn have feedback effects on the magnetization. We considered such a situation theoretically [13] for example in connection with the FM resonance from composite multiferroics with the conclusion that under certain conditions, the magnetoelectric (ME) coupling has an effect similar to an effective additional unidirectional anisotropy that can be influenced by an electric field by virtue of the electric response. Recent experiments for a Co/BaTiO3 interface [14] seem to confirm our predictions. Superparamagnetic behaviour of this structure is expected thus to be highly sensitive to ME coupling, even if this coupling is weak. It is worthwhile noting that so far, a major obstacle for the application of multiferroics is the smallness of the ME coupling. Hence, an efficient electric field control of magnetism is possible only in close proximity to the interface. In the present work we exploit two advantages: (1) we consider nanosystems where the aforementioned proximity is a major part of the whole object, and (2) we concentrate on a phenomenon that is influenced by the ME coupling in an exponential manner (because ME coupling acts as an additional anisotropy [13, 14]), thus circumventing the obstacle of a small ME coupling.

The purpose of the current study is to formulate the posed problem rigorously and to conduct numerical simulations to quantify the above statements and expectations. To this end, and to be specific, we consider Fe nanoclusters deposited on a FE substrate (BaTiO3); see figure 1.

Our analysis and numerical simulations confirm the above expectation that superparamagnetism in this composite structure can be controlled electrically and the size limit can be pushed down substantially. Our theory is based on the Fokker–Planck equation [15, 16] constructed for the Landau–Lifshitz–Gilbert (LLG) equation [17, 18] and yields Arrhenius-like exponential behaviour for the Néel relaxation time $T_N$ of the magnetization. Further numerical simulations on the thermodynamic properties for the coupled polarization and magnetization dynamics revealed an intimate relationship between the ME coupling strength and the superparamagnetic behaviour.

2. Theoretical model

The treatment of the coupling of a system to a thermal bath is an established case study for experiments and theory. In experiments, the thermal properties might be captured for example by the telegraph noise technique [19, 20], where the response of the system is measured as a function of time at different temperatures. For a two-state system, the number of switchings between the two stable states can be counted and to a 2-0 laminate multiferroic system in the terminology of [29]. To be specific, we perform concrete simulations of the FE BaTiO3 substrate and FM Fe nanoparticles. The density of these nanoparticles chosen is low enough that inter-nanoparticle couplings can be ignored. For this system it has been shown theoretically [30–32] and demonstrated experimentally [33, 34] that the ME coupling originating from the spin-polarized screening charges at the FE/FM interface [35] is large and stable even at room temperature [31]. In view of the already realized experiment [36], it is well conceivable that the suggested system in figure 1 is readily realizable, for example by increasing the annealing temperature for 26 monolayers of Fe on the BaTiO3 (1 0 0) substrate, which results in the formation of Fe nanoclusters on BaTiO3 with sizes from 30 to 150 nm. The construction of an analytical model based on the Fokker–Planck equation for FM nanoparticles in a multilayer can be ignored. Here, we focus on small FM nanoparticles, where a single-domain state is prevalent. The purpose of the current study is to formulate the posed problem rigorously and to conduct numerical simulations to quantify the above statements and expectations. To this end, and to be specific, we consider Fe nanoclusters deposited on a FE substrate (BaTiO3); see figure 1.
the Ginzburg–Landau–Devonshire (GLD) potential, widely accepted that temperature affects the coefficients of the equation of motion stresses the Landau–Lifshitz potential due to the ME coupling. Note that because of the latter term contributions to the FM or FE MFPT can be calculated. The treatment of thermal effects in FE materials may occur in a collinear manner. For an FM nanoparticle to be in a single-domain state, contributions from the exchange, the magnetocrystalline anisotropy and the FM dipole–dipole interactions should be compared [53, p 267]. Coherent magnetization switching takes place for the sizes when the exchange interaction exceeds the dipolar interactions (exchange length).

Zero-field thermal stability of ferromagnets and ferroelectrics. As depicted in figure 1, the FE substrate is macroscopically large and possesses a stable polarization \( P \equiv P_z \), which is aligned along the \( z \)-axis (tetragonal phase for BaTiO$_3$ [52], for a temperature range from 273 to 392 K). The Fe nanoparticles are of such a size that they are at the verge of the superparamagnetic limit (or below) and their density is such that no interactions between them need to be considered. Hence, it suffices to consider the dynamics of one of these nanoclusters. To be able to compare the numerical results with analytical findings, the FM nanoparticles should be in a single-domain state and the magnetization switching should occur in a collinear manner. For an FM nanoparticle to be in a single-domain state, contributions from the exchange, the magnetocrystalline anisotropy and the FM dipole–dipole interactions should be compared [53, p 267]. Coherent magnetization switching takes place for the sizes when the exchange interaction exceeds the dipolar interactions (exchange length). To fulfill the above restrictions the diameter of the iron nanoparticle should be around \( d_{\text{FM}} = 10 \text{ nm} \) [53].

The importance of surface effects in small FM nanoparticles is well recognized [54]. The pioneering experiment on bcc-iron nanoparticles with sizes from around 2 to 7 nm [55] suggested a particle diameter (\( d \))-dependent scaling law for the total anisotropy \( K_{\text{eff}} = K_{\text{bulk}} + 6K_{\text{surf}}/d \). Since then, numerous theoretical studies were conducted [56–60] revealing complex static and dynamical properties of the surface magnetization, in particular in relation to the influence of surface anisotropy. To account for these effects, a model based on classical Heisenberg spins [56–60] is more appropriate than the present approach. Here, we focus on the issue of magnetization stability of the Fe nanoparticles against thermal fluctuations, and calculate the MFPTs.

In the absence of a magnetic field the FM MFPT is given by [40]

\[
\tau_{\text{MFPT}}^{\text{FM}} = \frac{\tau_N \sqrt{\pi}}{(K_{\text{eff}}/k_B T)^{3/4}} e^{K_{\text{eff}}/k_B T},
\]

where \( K_{\text{Fe}} = 4.8 \times 10^4 \text{ J m}^{-3} \) is the magnetocrystalline anisotropy strength, the FM volume is \( V_{\text{FM}} = \pi d_{\text{FM}}^3/6 \) and the free diffusion time is defined as \( \tau_N = V_{\text{FM}} M_S (1 + \alpha_{\text{FM}}^2)/2 \gamma \alpha_{\text{FM}} K_{\text{eff}} \) [40]. The value of the damping parameter is \( \alpha_{\text{FM}} = 0.02 \) [61]. The saturation of the Fe magnetization is \( M_S = 1.71 \times 10^6 \text{ A m}^{-1} \) [53].

For an iron nanoparticle with the given constants and volume, at \( T = 293 \text{ K} \) we have

\[
\tau_{\text{MFPT}}^{\text{FM}} (d_{\text{FM}} = 10 \text{ nm}) \approx 9 \times 10^{-7} \text{ s}.
\]

The result of the MFPT derived from the Fokker–Planck equation constructed for an overdamped one-dimensional equation of motion [16, 22] can easily be applied to equation (5), which has the same form for the \( z \)-component of the polarization. At these conditions (\( T = 293 \text{ K}, V_{\text{FE}} = d_{\text{FE}} \times l \times l, \) where \( d_{\text{FE}} \) is the thickness of the FE and \( l \times l \) is its cross-section) and in the high barrier limit for the FE potential of BaTiO$_3$ (\( |\alpha_{\text{FE}}| = 2.77 \times 10^7 \text{ V m C}^{-1} \)) [62],
\[ \beta_{\text{FE}} = 1.7 \times 10^8 \text{ Vm}^5 \text{ C}^{-3} [62] \]

\[ F_{\text{FE}} = -\frac{\alpha_{\text{FE}}}{2} p^2 + \frac{\beta_{\text{FE}}}{4} p^4, \quad (9) \]

the zero-electric field FE MFPT can be estimated as

\[ \tau_{\text{MFPT}}^{\text{FE}} = \frac{\pi}{\sqrt{2}} \frac{\gamma_1}{\alpha_{\text{FE}}} e^{\frac{\beta_{\text{FE}}}{4\alpha_{\text{FE}}}} \approx 4 \times 10^{18} \text{ s}. \quad (10) \]

The comparison of equations (8) and (10) clearly demonstrates the stability of the FE layer against thermal noise, meaning that on the time scale of the experiment the FE substrate does not switch upon thermal noise.

In real experiments, however, FE might need to be attached to metallic electrodes, which results in depolarizing fields [45,64–66]. The FE barrier constant should then be modified according to [45]

\[ \bar{\alpha}_{\text{FE}} = -\alpha_{\text{FE}} + \frac{2d_{\text{int}}}{d_{\text{FE}} \varepsilon d_{\text{int}}}, \quad (11) \]

where \( d_{\text{int}} \approx 1 \text{ nm} \) is the thickness of the so-called ‘dead’ layer (screening length) [66] and \( \varepsilon_{\text{int}} = 100 \) is its dielectric constant.

Such small modifications of \( \alpha_{\text{FE}} \) can significantly change the FE MFPT. Thus, for \( d_{\text{FE}} = 100 \text{ nm} \) and \( l = 5 \text{ nm} \) we find for the FE MFPT from equation (10) with equation (11)

\[ \tau_{\text{MFPT}}^{\text{FE}} \approx 1 \text{ s}. \]

Comparing equations (8) and the FE MFPT estimate including depolarizing fields we may safely say that the FE substrate is not perturbed by heat and we do not need to consider thermal fluctuations in equation (5).

3. Numerical simulations

From the theory of magnetization dynamics at finite temperatures [24], the FM MFPT at finite applied static magnetic fields is known. The switching time, which is defined as \( \tau_{\text{FM}} = 2(1 / \tau_{\text{N}} + 1 / \tau_{\text{MP}})^{-1} \) then in the presence of a reduced static magnetic field \( b = \frac{1}{2} \mu_0 M_{\text{S}} \frac{H}{M_{\text{S}}}; \)

\[ \tau_{\text{FM}}^{\text{FE}} = \frac{\tau_{\text{N}} \sqrt{\pi}}{2} \left( \frac{K_1}{J_0} \right)^{\pi/2} \left( 1 + b^2 \right) \left( 1 + b \right)^{-\pi/2} \left( 1 + b^2 \right)^{-1/2} \left( 1 - b \right)^{\pi/2} \left( 1 + b \right), \quad (12) \]

\[ \tau_{\text{FM}}^{\text{MFPT}} \]

Here, times \( \tau_{\text{MP}}^{\text{MFPT}} \) and \( \tau_{\text{FM}}^{\text{MFPT}} \) denote the MFPTs for the classical magnetization \( M(t) \) depending on the orientations of the applied magnetic field and the initial magnetization \( M(0) \).

As discussed in previous studies [13,30,67,68] the ME coupling at the FE/FM interface is due to a spin-polarized charge rearrangement (screening) and can be modelled by \( EC/(VC) = \lambda P_1 \cdot M \), where \( \lambda \) is a pseudoscalar characterizing the strength of this coupling, and \( P_1 \) is the polarization at the FM interface.[6] The FM system is considered

6 We neglect effects of the external electric field on the metallic ferromagnetic part of the system.

Figure 2. Influence of the strength of ME coupling \( \lambda \) on the averaged switching time \( \tau_{\text{FM}}^{\text{MFPT}} \) of the magnetization. The diameter of the FM nanoparticle is \( d_{\text{FM}} = 10 \text{ nm} \). The absolute value of the anisotropy energy for the whole nanoparticle is \( K_1 V \approx 2.5 \times 10^{-20} \text{ J} = 1.5 \text{ eV} \). The ratios for the minimum (250 K) and the maximum (400–450 K) temperatures shown on the graph scale are \( K_1 V/(k_B T_{\text{MAX}}) = 7.3 \) and \( K_1 V/(k_B T_{\text{MAX}}) = 4.1 \), respectively. Symbols represent numerical simulations, whereas the coloured curves follow from equation (12) with the effective field taken as \( b \sim \lambda P_1 / B_{\text{A}} \), where \( B_{\text{A}} = 2K_1 / M_\text{S} \). No external electric or magnetic fields are applied. Due to computational limitations, the maximum length of the time scale (related to the experimental measurement time) is set to 20 \( \mu \)s. The other parameters are listed in the text. Inset schematically shows the initial magnetization state (arrow up) and the change of the free energy \( \Delta F / \Sigma_1 \) depending on the orientations \( \theta \), being the averaged switching time \( \tau_{\text{FM}}^{\text{MFPT}} \).
full quantitative and qualitative agreement with the analytical results inferred from equations (7) and (12).

We first inspect the influence of the strength of ME coupling on the behaviour of FM switching times (figure 2). The switching times are presented as a function of temperature, which is one of the natural external parameters assisting the switching. Because of the parallel alignment of the magnetization and the polarization, increasing \( \lambda \) results in the negative effective magnetic field \(-\lambda P_z\), which elevates the initial state of \( M \) and hence lowers the overall switching time (inset of figure 2). In addition, switching times obtained numerically and from equation (12) show a good agreement in the chosen range of applied fields and temperatures, indicating the possibility of fitting the experimental data with analytical expressions, based on equation (12) for example.

Figure 2 demonstrates a general dependence of switching times on moderate \((<0.1 \text{ s}^{-1})\) and strong \((0.3 \text{ s}^{-1})\) values of ME coupling. Let us consider the case of a finite ME coupling strength \( \lambda = 0.06 \text{ s}^{-1} \) [68]; this value is based on the \textit{ab initio} calculations. We find that the FM switching times are sensitive to the applied electric field \( E_z \) (figure 3). In particular, the direction of the electric field is decisive; i.e. once the electric field is operational (red and blue points in figure 3), visible changes in the FM switching times are observed.

An essential finding depicted in figure 4 is that, for a fixed particle size, the switching time can be modified by more than an order of magnitude by the ME coupling assisted by an electric field. In other words, the size of particles with the same switching time can be decreased substantially by ME coupling. In fact, particles that are already superparamagnetic can be stabilized by ME coupling. This fact can in turn serve as an indicator for ME coupling; in particular, the dependence of the applied external electric field. This strong dependence is consistent with the fact that the switching time depends in general exponentially on the energy barrier that is modified by ME coupling (see [16] for a discussion of the physics behind the exponential behaviour).

In addition to switching times, the calculations of hysteresis were performed for the temperature range from zero to about 400 K (figure 5). The temperature dependence of the net magnetization for the system of iron nanoparticles embedded into a BaTiO3 matrix (3-0 multiferroic system in the terminology of [29]) was previously reported in [11]. Since thermal fluctuations assist the magnetization switching process, the result is a reduction of the coercive fields. A relatively low frequency \( \omega/(2\pi) = 0.01 \text{ GHz} \) corresponding to a period of \( T = 100 \text{ ns} \) was chosen to provide sufficient relaxation, whereas the relaxation time of the nanoparticle is mainly governed by the damping parameter and scales according to \( T_{rel} \approx T_A/\alpha_{FM} = 2\pi M_S/\gamma 2K/\alpha_{FM} \approx 33 \text{ ns} \). Additionally, we observe a small shift of hysteresis curves due to the presence of a unidirectional anisotropy induced by the ME coupling. For the linear ME coupling this effect is supposed to be similar to the exchange bias effect [71], which is sizeable for FM nanoparticles.

4. Discussion and conclusions

We considered in this work the superparamagnetic behaviour of composite multiferroics, with a special focus on Fe nanoslands multiferroically coupled to BaTiO3. For realistic material parameters we demonstrated that a Fe magnetization switching is feasible via external electric fields which should be experimentally realizable by means of telegraph noise. An important finding is that the FM switching times, expressed as MFPTs [24], can be tuned by orders of magnitude (figure 3) by ME coupling and electric fields acting on the FE polarization. Our theoretical tools included analytical results and numerical simulations. We stress that the analytical formulae (e.g. equation (12)) should be taken as a first guess since the analytical derivations are based on numerous approximations, for example on the high energy barrier limit and absorbing boundary conditions, meaning that multiple barrier crossings are not possible. In particular, figure 2 shows that as long as the
ME coupling is small ($\lambda < 0.1 \text{ s F}^{-1}$), analytical results and simulations are in good agreement (see dots and curves). From telegraph noise experiments performed on such systems, one may determine the values of the ME coupling, assuming that it is linear. In this case we expect that a fitting of the switching time as a function of the temperature according to equation (12) should be achievable. By switching the polarization direction, one can derive the value of the effective field induced by the ME coupling and finally relate it to the ME coupling constant from equations (7) and (12). We stress, however, that in general equation (12) is symmetric with respect to the applied $b$ field; therefore, in order to obtain sizeable effects experimentally, one should fix the initial magnetization state, for example by an external applied magnetic field. It should also be emphasized that the so-called pinning site effects reported in [72–74] will not strongly modify the results reported here, since the ferroelectricity is controlled by a strong electric field, which indirectly acts on the magnetization.

Further forms of the ME coupling, whose occurrence depends on the particularity of the composite structures, might modify the obtained results. For example, assuming that the ME coupling energy has an additional contribution that scales as $\lambda_1 P_1 M^2$, then the total effective field acting on the magnetization additionally attains a term that is linear in magnetization. This would lead to the modification of the height of the energy barrier defined by the magnetocrystalline anisotropy strength $K_1$. When the magnetization is aligned along the $z$-direction, the coupling with $\lambda_1$ will result in a modification of the prefactor $K_1 V_{FM}/(k_B T)$ in equation (12). Further contributions like $\lambda_2 \lambda_3 (P_1 \cdot M)^2$ may modify equation (12) in a similar way with a different strength of the net ME coupling.

The final remark concerns the form of the FM nanoparticles, which in general might have a form different from an ideal sphere leading to the effect of sufficiently strong demagnetizing fields [53, 75]. The presented results rely on the idealization of flat nanoparticles (demagnetizing factor $N_r = 1$), giving rise to an axially symmetric contribution to the FM free energy (equation (13)) and thus correcting the total effective field acting on the magnetization. An elliptical form of FM nanoparticles (especially with a high or low ratio of major ellipsoid axes $c/a$) will lead to a non-axially symmetric FM free energy contribution. Experimentally, following the procedure of [36] on Fe/BaTiO$_3$ while lowering Fe coverage, our proposal in figure 1 should be well within reach.

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**References**

[1] Weller D and Moser A 1999 IEEE Trans. Magn. 35 4423
[2] Néel L 1949 Ann. Geophys. 5 99
[3] Skumryev V, Stoyanov S, Zhang Y, Hadjipanayis G, Givord D and Nogues J 2005 Nature 423 850
[4] Laurens S, Dutz S, Häfele U O and Mahmoudi M 2011 Adv. Colloid Interface Sci. 166 8
[5] Romero Gómez J, Ferreiro García R, DeMiguel Catoira A and Romero Gómez M 2013 Renew. Sust. Energy. Rev. 17 74
[6] Weinstein J S, Varallyay C G, Dosa E, Gahramanov S, Hamilton B, Rooney W D, Muldoon L L and Neuwelt E A 2010 J. Cereb. Blood Flow Metab. 30 15
[7] Fiebig M 2005 J. Phys. D: Appl. Phys. 38 R123
[8] Eerenstein W, Mathur N D and Scott J F 2006 Nature 442 759
[9] Ramesh R and Spaldin N A 2007 Nature Mater. 6 21
[10] Nan C-W, Bichurin M I, Dong S-X, Viehland D and Srivivasan G 2008 J. Appl. Phys. 103 031101
[11] Borges R P, da Silva R C, Cruz M M and Godinho M 2010 J. Phys.: Conf. Ser. 200 072014
[12] Sone K, Sekiguchi S, Naganuma H, Miyazaki T, Nakajima T and Okamura S 2012 J. Appl. Phys. 111 124101
[13] Sukhov A, Horley P P, Jia C-L and Berdarad J 2013 J. Appl. Phys. 113 013908
[14] Jedrcy N, von Bardeleben H J, Badjeck V, Demaille D, Stanescu D, Magnan H and Barbier A 2013 Phys. Rev. B 88 121409(R)
[15] Fokker A D 1914 Ann. Phys. 43 810
[16] Risken H 1989 The Fokker–Planck Equation (Berlin: Springer)
[17] Landau L D and Lifshitz E M 1935 Phys. Z. Sowjetunion 8 153
[18] Gilbert T L 1955 Phys. Rev. 100 1243 (abstract only)
[19] Gilbert T L 2004 IEEE Trans. Magn. 40 3443
[20] Campbell P M, Snow E S, Moore W J, Glembocki O J and Kirchofer S W 1991 Phys. Rev. Lett. 67 1330
[21] Wernsdorfer W, Bonet Onorozo E, Hasselbach K, Benoit A, Barbara B, Demoncy N, Loiseau A, Pascard H and Amilery D 1997 Phys. Rev. Lett. 78 1791
[22] Langevin P 1908 C.R. Acad. Sci. 146 530 (in French)
[23] Leons D S and Gythiel A 1997 Am. J. Phys. 65 1079 (Engl. transl.)
[24] Hänggi P, Talkner P and Borkovec M 1990 Rev. Mod. Phys. 62 251

![Figure 5](image_url)
