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# Adiabatic magnetothermia makes possible the study of the temperature dependence of the heat dissipated by magnetic nanoparticles under alternating magnetic fields

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Determining the low-temperature dependence of the specific absorption rate (SAR) of magnetic nanoparticles under alternating magnetic fields with amplitudes and frequencies similar to those used in applications such as magnetic fluid hyperthermia, becomes essential when theoretical expressions fail to extrapolate the behavior of nanoparticle arrangements. We prove that adiabatic magnetothermia is capable of providing SAR($T$) data displaying an excellent continuity with those obtained from magnetic measurements at lower ac-field amplitudes and frequencies. © *2011 American Institute of Physics*. [doi:10.1063/1.3600633]

Very active research about the use of magnetic nanoparticles (MNPs) in biomedicine is arising from biological applications, like magnetic fluid hyperthermia (MFH) for cancer treatment, or the thermally assisted drug release, based on the capability of such nanomaterials for dissipating heat when they are subjected to alternating magnetic fields.[1–3] A key factor for this research is to accurately measure the specific absorption rate (SAR), defined as the heat power released per gram of magnetic material upon ac-field application. Even if MNPs operate between 36 and 45 °C in these applications, the study of the low-temperature dependence of the released power derives relevant information to be used to correlate SAR, material properties, and ac magnetic field parameters, providing physical data about the different dissipation mechanisms that may activate at this nanoscale,[2] as well as feedbacks to synthetic groups. Studies of the power-dissipation temperature dependence of MNPs are currently tackled by magnetic methods, where the heat dissipation mechanism must be taken into account. The SAR of ferromagnetic MNPs can be determined from minor magnetization loops.[4–6] This method cannot be, however, applied to superparamagnetic nanoparticles, which do not show hysteresis loops, but SAR can be obtained from the measurement of the out-of-phase ac magnetic susceptibility, $\chi''$, by using the theoretical expressions that relate both magnitudes.[7] One drawback of the latter method is that, due the characteristics of the currently used setups, $\chi''$ is often measured with ac-field parameters different than those used for MFH.[8,9] This implies the necessity of extrapolating the results to the right amplitudes and frequencies, which may derive incorrect results, given that the SAR variation with $H_0$ and $f$ depends on the material characteristics, dissipation mechanism, presence of dipolar interactions, etc., and that in some cases there are considerable disagreement between experimental data and most common theoretical predictions.[10–13] We present herein an alternative method to avoid the use of extrapolations, that is, the low-temperature calorimetric SAR characterization of MNPs, performed in adiabatic conditions at field amplitudes and frequencies typical of MFH, and within the biological range of ac-field application ($H_0 \times f \leq 485$ kHz×kA/m).[14]

We studied a magnetite/epoxy nanocomposite obtained from a commercial ferrofluid (Ocean Nanotech) and the epoxy resin Epofix™. It contained 17.9 mg of magnetite and 76.6 mg of resin. This composite allowed, with respect to the ferrofluid, obtaining a fix MNP distribution, avoiding the phase transition of the dispersive medium in the temperature range considered. The magnetite MNPs were found to be highly monodisperse with a particle diameter of $10.7 \pm 0.8$ nm, as determined by transmission electron microscopy. According to their composition and size, MNPs are well under the magnetic single-domain/multidomain limit and small enough as to display superparamagnetism at certain temperature range.

The volumetric power dissipation due to the magnetic work done on a system in an adiabatic process can be expressed, for small magnetic field amplitudes, as $P = \mu_0 \pi \chi'' f H_0^2$, where $\mu_0$ is the magnetic permeability of free space. Then, the SAR of that system can be expressed as SAR $= \mu_0 \pi \chi'' f H_0^2 / \rho$ (in SI units), where $\rho$ is the mass density of the MNPs. For MNPs displaying superparamagnetism and, for a noninteracting monodisperse particle assembly, $\chi'' = \chi_0 \omega\tau / [1 + (\omega\tau)^2]$, where $\omega = 2\pi f$, $\chi_0$ is the equilibrium susceptibility, and $\tau$ is the effective relaxation time of the thermally induced magnetic-moment relaxation mechanisms.[7] If particles are not free to move within the sample, then $\tau$ stands for the Néel relaxation time, defined as $\tau = \tau_0 \exp[E_b / (k_B T)]$, where $\tau_0 = 10^{-8} - 10^{-10}$ s, $E_b$ is the energy barrier for the magnetic moment reversal, given by the product of the magnetic anisotropy and the magnetic volume (V) of the MNPs, and $k_B$ is the Boltzmann constant. The $\chi''(T)$ function presents a maximum when $\omega\tau = 1$ at $T_b = -E_b / [k_B \ln(2\pi f \tau_0)]$, the blocking temperature, which depends on the excitation frequency. Furthermore, for small magnetic field amplitudes, $\chi_0 \cong (\mu_0 M_s^2 V) / (3 k_B T)$ (in SI units), where $M_s$ is the saturation magnetization of the MNPs, and consequently, $\chi''$ does not depend on $H_0$. According to these theoretical expressions, the SAR of a sample

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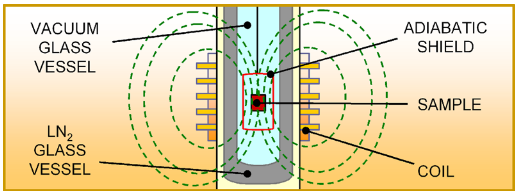


FIG. 1. (Color online) Partial scheme of the adiabatic magnetothermal setup.

with fixed non-interacting MNPs should present the same thermal behavior than $\chi''(T)$, depend on $H_0^2$ and vary with $f$ as $f^2/[1+(2\pi\tau)^2 f^2]$, that is, for $T \ll T_b$, where $\omega\tau \gg 1$, SAR should not depend on $f$, and for $T \gg T_b$, where $\omega\tau \ll 1$, SAR should vary as $f^2$.

At determining SAR by calorimetric methods, thermal dissipation mechanisms do not need to be considered *a priori* since only the effect of heating is measured; the temperature increment, $\Delta T$, experimented by a specimen due to the heat dissipated by the MNPs contained in it upon application of an ac-magnetic-field pulse. The formula that allows calculating SAR from the measuring of $\Delta T$ is $\mathrm{SAR}=(1/m_{\mathrm{MNP}}) \times C \times (\Delta T/\Delta t)$, where $m_{\mathrm{MNP}}$ is the mass of magnetic material, $C$, the heat capacity of the whole sample, and $\Delta t$, the duration of the ac-magnetic-field. The use of this equation requires that all generated heat is invested in the sample temperature raise, that is, adiabatic measuring conditions. Otherwise, $\Delta T$, and, consequently, SAR, will be underestimated.[15] Using a recently developed adiabatic magnetothermal setup,[16] in which heat losses are minimized by enclosing the sample (and the ceramic shield that controls radiation and conduction losses) in a vacuum environment by means of a sealed glass vessel, the measurement of *SAR* at subambient temperatures was possible after previous cooling of the sample environment. To achieve this cooling, the setup was provided of another glass vessel (see Fig. 1), surrounding the former, that was filled with liquid nitrogen once the final vacuum pressure was reached, allowing a slow and safe cooling of sample and shield. Once they were cold, $\Delta T$ values were recorded upon heating runs. Given that the sample owns no external heating means but its temperature increases only due to its own heat dissipation, the heating ramps were obtained by applying as many successive ac-field pulses [Fig. 2(a)] as to provide enough temperature increments to drive the sample to room temperature. From each ac-field pulse

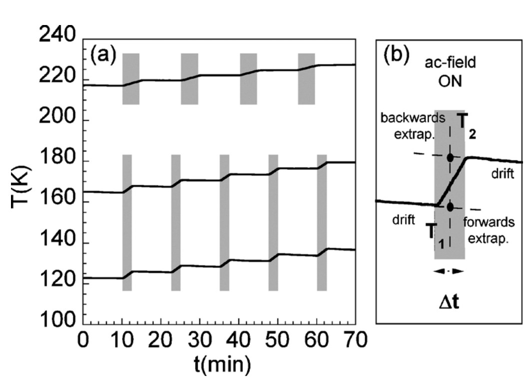


FIG. 2. (a) Heating ramps obtained by applying successive ac magnetic field pulses. The gray areas indicate the field application intervals, $\Delta t$. (b): calculation of $\Delta T = T_2 - T_1$, by extrapolation of the temperature drifts before and after ac-field application.

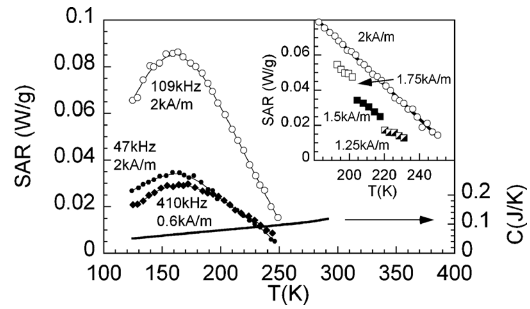


FIG. 3. Sample heat capacity, $C(T)$, (line). Temperature dependence of SAR under different ac magnetic field parameters. Inset: detail of the linear-fitted series at 109 kHz and 2 kA/m, together with partial series at the same frequency and different ac magnetic field amplitudes.

[Fig. 2(b)], one $\Delta T$ value at a given temperature was calculated as $\Delta T = T_2 - T_1$, where $T_2$ and $T_1$ are, respectively, the backward and forward extrapolation of the temperature drifts after and before the ac-field application, at the midpoint of $\Delta t$. The $\Delta T$ so obtained was assigned to the temperature $T=(T_2+T_1)/2$.

To describe the SAR variation with temperature, the temperature dependence of $C$ (Fig. 3) must also be taken into account. $C = m_{\mathrm{MNP}} \times c_{p,\mathrm{MNP}} + m_{Epoxy} \times c_{p,\mathrm{Epoxy}}$, where $m_{\mathrm{Epoxy}}$ is the mass of the epoxy resin within the sample, and $c_{p,\mathrm{MNP}}$ and $c_{p,\mathrm{Epoxy}}$, stand for the specific heat capacity of the magnetic material and the epoxy resin, respectively. $c_{p,\mathrm{Epoxy}}$ was determined using a differential scanning calorimeter (DSC, TA Instruments), and the temperature dependence of $c_{p,\mathrm{MNP}}$, was taken from literature data.[17]

The temperature dependence of SAR, constructed from these $C$ data and the $\Delta T/\Delta t$ trends, is also shown in Fig. 3. Three complete temperature series were performed at frequencies of 47 kHz, 109 kHz, and 410 kHz, and at $H_0$ values of 2 kA/m, 2 kA/m, and 0.6 kA/m, respectively. Also, in order to obtain the experimental SAR dependence on $H_0$, partial series at $H_0$=1.75, 1.5 and 1.25 kA/m, for $f$ =109 kHz were performed (inset in Fig. 3). Measurements between 190 and 235 K for 109 kHz were linear-fitted and the data from the fit were compared. SAR was found to be proportional to $H_0^{\mathrm{n}}$, with $\mathrm{n}=1.98 \cong 2$, so data fit well to the quadratic relationship predicted by theory. Taking into consideration this dependence, data in Fig. 3 can be scaled to the same field amplitude to study the influence of $f$ in SAR. If we compare these scaled data, for example, at 240 K, where $T \gg T_b$ and SAR should vary as $f^2$, we found that SAR presents a much softer dependence on $f$ than expected. This fact should be also reflected in $\chi''$.

The thermal dependence of $\chi''$ was performed on the same specimen used for SAR determination through magnetic ac susceptibility measurements, using commercial Quantum Design magnetometers, namely, a magnetic property measurement system (MPMS) for $2 \le f \le 852$ Hz and a physical property measurement system (PPMS) for $1 \le f \le 10$ kHz, all with $H_0 = 4$ Oe ($\cong 0.32$ kA/m). Figure 4 collects some of these trends, one for each frequency decade, together with those obtained from SAR measurements (at 47 and 410 kHz) as $\chi''(\mathrm{emu/g\ Oe}) = \mathrm{SAR} \times 10^6/(4\pi^2 \mu_0 f H_0^2)$, where the magnitudes at the right part of the equation are expressed in SI units.

It must be pointed that the temperature dependence of $\chi''$ obtained from adiabatic SAR measurements at frequencies

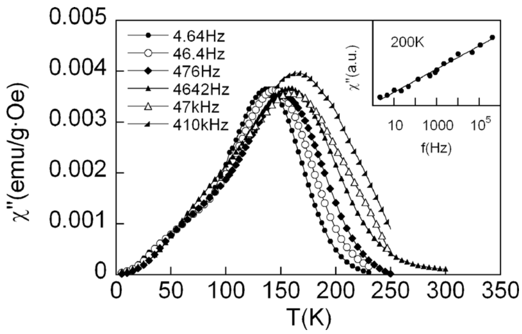


FIG. 4. Temperature dependence of the out-of-phase ac magnetic susceptibility at various frequencies obtained from magnetic measurements (MPMS, 4.64–476 Hz, and PPMS, 4642 Hz) and from SAR (47 and 410 kHz). Inset: Variation in the out-of-phase ac susceptibility with frequency at 200 K.

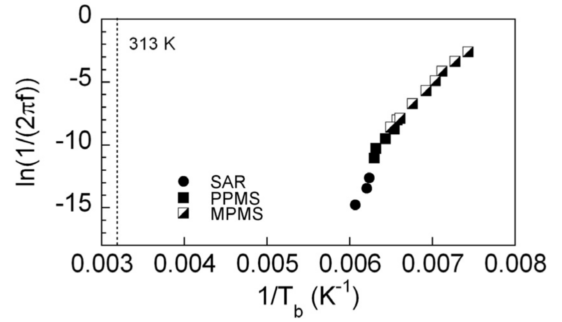


FIG. 5. $\ln[1/(2\pi f)]$ vs $1/T_b$ obtained from magnetic and SAR measurements.

typical of MFH follows extraordinary well, in shape, position, and absolute value, the trend of the $\chi''(T)$ curves determined from magnetic measurements at lower $H_0$ and $f$ values, validating the use of this calorimetric technique at low temperature.

Also, the dependence of $\chi''$ with frequency reflects the presence of magnetic interactions between MNPs, fact that invalidates the use of the theoretical expressions for noninteracting nanoparticles for describing our assembly. Below $T_b$, there is a very weak dependence of $\chi''$ with $f$, characteristic of interacting assemblies.[18] Above $T_b$, if we consider the values of $\chi''$ at 200 K (inset in Fig. 4), we should expect a linear dependence with $f$ $(T \gg T_b)$, but instead, the experimental data can be fitted to a logarithmic one. Studies on superspin glasses,[11] i.e., ensembles of single-domain particles with non-negligible interparticle interactions and displaying a kind of collective state, reflect that the variation in $\chi''$ with $f$ presents several regimes. In particular, for small and high $\omega\tau$ values, $\chi'' \propto \omega\tau$ and $\chi'' \propto (\omega\tau)^{\beta/z\upsilon}$, respectively, where $\beta$ and $z\upsilon$ are critical exponents. Our case seems to lay in the transition range between both regimes, in which the $\chi''$ versus $f$ dependence is logarithmic. Again, data obtained from SAR measurements fit really well in the trend. Eventually, the position of the maxima of $\chi''$ scarcely changes with the excitation frequency. The measurements have been performed with frequencies ranging between 2 Hz and 410 kHz, that is, six orders of magnitude in $f$, and the position of the maximum has only be shifted by 30 K. For noninteracting MNPs, $T_b$ is related to $f$ as $\ln[1/(2\pi f)] = \ln(\tau_0) + (E_b/k_B) \times (1/T_b)$, that is, is linear with $1/T_b$. Within this representation, Fig. 5 shows that data calculated from SAR measurements shows a very good continuity with magnetic data. The observed trend displays a very pronounced slope, that, fitted to a straight line, would provide a very small and unphysical intersection with the ordinate axis, result that corroborates the presence of quite strong interactions between MNPs.[19] Our data even deviate from a straight line, invalidating the possibility of extrapolating the frequency behavior of the sample with the above expression.

In conclusion, we have introduced the temperature as a variable in the study of the SAR of MNPs as determined by adiabatic magnetothermia. All the results obtained from this technique have shown an excellent continuity with the data obtained from ordinary magnetic measurements at lower ac-field amplitudes and frequencies. Finally, it has been demonstrated that SAR data cannot be easily reproduced in our case by extrapolation of the magnetic data through most currently used theoretical expressions, due to the presence of magnetic interactions within the sample.

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