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## Oscillating adiabatic temperature change of 2D diamagnetic materials

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## ABSTRACT

Studies on magnetocaloric effect generally concern ferromagnetic materials, due to their high magnetocaloric potential near phase transitions. Recently, this effect on diamagnetic materials was explored and oscillations on the entropy change observed as a consequence of the crossing of the Landau levels through the Fermi energy. The present paper explores the adiabatic temperature change in graphenes and thin films of non-relativistic diamagnetic materials and then compares the results with those from 3D diamagnets. Applying 10 T of magnetic field, the temperature change of a gold thin film reaches 1 K, while for bulk gold the temperature change is smaller than 6 mK. For graphenes, the temperature change reaches 4 K with a field of  $\sim 1$  T.

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## 1. Introduction

Magnetocaloric effect (MCE) is a thermal response of materials to a magnetic field change. The effect is induced by a change in the field dependent part of the entropy that enables the material to exchange heat with a thermal reservoir, under isothermal conditions, or even change its temperature, under adiabatic conditions. Applying a field change  $\Delta B : B_i \rightarrow B_f$  to the material, the quantities that characterize the effect are as follows: the entropy change ( $\Delta S = S(T, B_f) - S(T, B_i)$ ), related to the heat exchange ( $\Delta S = \Delta Q/T$ ) under an isothermal process; and the temperature change ( $\Delta T = T_f - T_i$ ) in an adiabatic process, which is ruled by the condition  $S(T_i, B_i) = S(T_f, B_f)$ .

The idea of using the MCE for refrigeration purposes was first suggested by Debye [1] and Giauque [2] in the late 1920s. The process known as adiabatic demagnetization allowed the achievement of ultra-low temperatures. Another important step for magnetic refrigeration came in 1976, when Brown proposed and constructed a device that is able to work near room temperature [3]. Such device produced a temperature difference of 46 °C to  $-1$  °C between the hot and cold parts. Almost 20 years ago, the discovery of the giant MCE [4] stimulated research on magnetocaloric materials and made magnetic refrigeration a promising technique.

As an important quantity for the MCE, the entropy change can be expressed as

$$\Delta S(T, \Delta B) = \int_{B_i}^{B_f} \left. \frac{\partial M}{\partial T} \right|_B dB. \quad (1)$$

The above equation shows that the entropy change is larger when the magnetization is most affected by temperature changes, and such situation occurs close to phase transitions. For this reason, materials with some magnetic ordering, like ferro, antiferro and ferrimagnets, have been widely studied.

Recently, magnetocaloric properties of diamagnetic materials were studied and oscillations were found due to the crossing of the Landau levels through the Fermi energy; a mechanism similar to the one that causes oscillations on the magnetization – the so-called de Haas–van Alphen effect. Both isothermal [5] and adiabatic [6] processes were studied in 3D diamagnets, while the magnetic entropy change was evaluated for those with 2D character: graphene [7], a relativistic material, and a thin film of non-relativistic behavior [8].

The present paper deals with two-dimensional materials in adiabatic conditions to complete the set of magnetocaloric properties, where the basic model used was a non-interacting electron gas. In the next sections we evaluate the temperature change for graphenes, firstly using a simple gas of Dirac electrons, and then we add the effect of scattering from impurities. In the following section, we treat a non-relativistic diamagnetic material. At last, we discuss the results comparing with those from 3D diamagnets, previously studied.

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## 2. Graphenes

The magnetic entropy per area of a graphene sheet is given by [9,7]

$$S(T, B) = S_0(T) + S_{osc}(T, B), \quad (2)$$

where  $S_0(T)$  is the field independent term and

$$S_{osc}(T, B) = 2Nk_B \frac{1}{m} \sum_{j=1}^{\infty} \frac{1}{j} \cos(jm\pi) \mathcal{T}(j\lambda), \quad (3)$$

is the oscillating field-dependent term. Above  $N$  is the density of charge carriers, and

$$m = \frac{N\phi_0}{B}, \quad (4)$$

is related to the magnetic field, where  $\phi_0 = \pi\hbar/e$  is the magnetic flux quantum. The thermal dependence of the entropy is contained in the function

$$\mathcal{T}(x) = \frac{xL(x)}{\sinh x}, \quad (5)$$

in which

$$L(x) = \coth x - \frac{1}{x}, \quad (6)$$

is the Langevin function. Finally,

$$x = \frac{m}{N} 2\pi\sqrt{N\pi} \frac{k_B T}{\hbar v_F}, \quad (7)$$

and  $v_F$  is the Fermi velocity. Note that both  $m$  and  $x$  are dimensionless.

To obtain the adiabatic temperature change we must know the zero-field contribution to the total entropy; and we can calculate it from the grand potential

$$S_0(T) = -\frac{\partial\Phi_0(T)}{\partial T}. \quad (8)$$

The grand potential reads as

$$\Phi_0(T) = -k_B T \int_0^{\infty} g_0(\epsilon) \ln(1 + ze^{-\beta\epsilon}) d\epsilon, \quad (9)$$

where  $z = e^{\beta\mu}$  is the fugacity and  $g_0(\epsilon)$  the density of states. In two dimensions, the density of states per area is [10]

$$g_0(\epsilon) = \frac{2k dk}{\pi d\epsilon}. \quad (10)$$

Above, we already included the factor of 4, which corresponds to spin and sublattice degeneracies [11]. Electrons in graphenes behave like relativistic massless particles; thus, they obey Dirac equation and, as a consequence, graphene has a linear dispersion relation near the Dirac point [12]

$$\epsilon = \hbar v_F k. \quad (11)$$

From the above dispersion relation, the density of states becomes

$$g_0(\epsilon) = \frac{2}{\pi(\hbar v_F)^2} \epsilon. \quad (12)$$

Once we know the density of states for a 2D gas of Dirac electrons, we use Eq. (9) to obtain the following expression for the grand potential in terms of the polylogarithm function

$$\Phi_0(T) = \frac{2k_B^3 T^3}{\pi(\hbar v_F)^2} Li_3(-z). \quad (13)$$

At low temperature,  $k_B T \ll \epsilon_F$ , the chemical potential approaches to the Fermi energy and  $z \approx e^{\beta\epsilon_F} \rightarrow \infty$ . Therefore, we can use the following expression for the polylogarithm function:

$$Li_n(-z) \approx -\frac{(\ln z)^n}{n!} - \frac{\pi^2 (\ln z)^{n-2}}{6(n-2)!} \quad \text{for } z \rightarrow \infty. \quad (14)$$

Thus, the grand potential becomes

$$\Phi_0(T) = -\frac{1}{3\pi(\hbar v_F)^2} (\mu^3 + \pi^2 k_B^2 T^2 \mu). \quad (15)$$

From the grand potential we also obtain the density of charge carriers

$$N = -\frac{\partial\Phi_0}{\partial\mu} = \frac{1}{3\pi(\hbar v_F)^2} (3\mu^2 + \pi^2 k_B^2 T^2), \quad (16)$$

and for  $T=0$ , we have the relationship between the Fermi energy and the density of charge carriers

$$\epsilon_F = \hbar v_F \sqrt{N\pi}. \quad (17)$$

Using the above relation we could rewrite Eq. (7) in a more compact form

$$x = 2\pi^2 m \frac{k_B T}{\epsilon_F}. \quad (18)$$

From Eqs. (8), (15) and (17), we finally obtain the zero-field entropy

$$S_0(T) = \frac{2\pi^2 N k_B^2 T}{3\epsilon_F}. \quad (19)$$

As stated before, it is possible to obtain the adiabatic temperature change from the condition

$$S(T_0, 0) = S(T_B, B). \quad (20)$$

Using Eqs. (2), (3) and (19), we find

$$\Delta T = T_B - T_0 = -6T_B \sum_{j=1}^{\infty} \cos(jm\pi) \frac{L(jx_B)}{\sinh(jx_B)}, \quad (21)$$

where  $x_B = x(T_B)$ . This is a self-consistent problem since the temperature change depends on the final temperature  $T_B = T_0 + \Delta T$ .

Fig. 1 presents the adiabatic temperature change as a function of  $m$ , inversely proportional to the magnetic field. The result was obtained with a self-consistent numerical calculation where the sum in Eq. (21) was carried out up to  $j=100$ . As a matter of comparison, the same calculation was performed up to  $j=1000$  (not shown), and the output was the same as the one shown in Fig. 1. Considering a typical value for the density of charge carriers in a graphene sheet [13]  $N = 10^{16} \text{ m}^{-2}$ , we observe the oscillatory behavior of the temperature change with an applied field  $B \approx 1 \text{ T}$ .

Fig. 2 presents the adiabatic temperature change as a function of the initial temperature  $T_0$ . We see that, at low temperatures, increasing  $T_0$  results in a larger temperature change up to a maximum value that depends on the applied magnetic field.

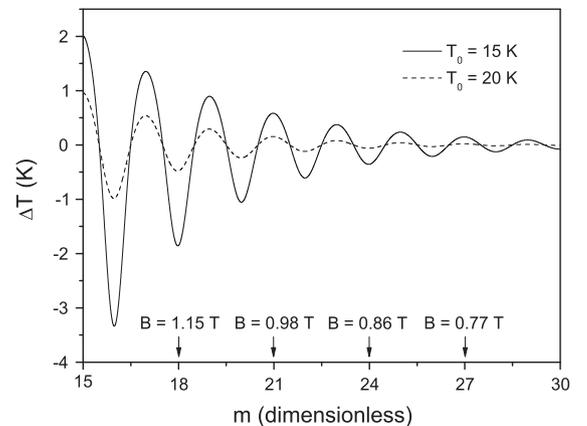


Fig. 1. Adiabatic temperature change in graphene as a function of  $m = N\phi_0/B$ . We obtained the assigned values of magnetic field considering  $N = 10^{16} \text{ m}^{-2}$  as the density of charge carriers.

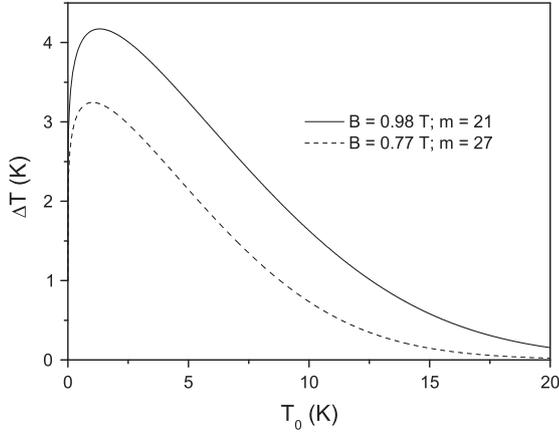


Fig. 2. Adiabatic temperature change in graphene as a function of the initial temperature  $T_0$ .

The values of magnetic field used correspond to the maxima of the oscillating pattern observed in Fig. 1. Increasing the initial temperature beyond the value of maximum  $\Delta T$  continuously reduces the temperature change.

### 3. Graphenes with impurities

We consider in this section the effect of scattering of electrons by some defect or impurity. This process is characterized by a scattering rate  $\Gamma$ . The consequence of the scattering is that the Landau levels are broadened [14], and the broadening is taken into account convoluting the density of Landau states with the Lorentz distribution  $P_\Gamma(\omega) = \Gamma / [\pi(\omega^2 + \Gamma^2)]$ . Thus, considering scattering, the density of states is found through

$$g_\Gamma(\varepsilon) = \int_{-\infty}^{\infty} P_\Gamma(\omega - \varepsilon) g(\omega) d\omega, \quad (22)$$

where  $\omega$  is an energy variable. The procedure and all the calculations to obtain the grand potential are already reported, for instance, in References [14,15]. The result is

$$\Phi_{osc}(T, B) = \frac{(eBv_F)^2}{\pi\varepsilon_F} \sum_{j=1}^{\infty} \frac{\cos(ju\pi)}{(j\pi)^2} \frac{jx}{\sinh(jx)} e^{-2\pi j m \gamma}, \quad (23)$$

where

$$u = \frac{\varepsilon_F^2 - \Gamma^2}{e\hbar v_F^2 B} = m(1 - \gamma^2), \quad (24)$$

with  $\gamma = \Gamma/\varepsilon_F$ . We need the magnetic entropy, which can be obtained from the grand potential above, and it reads as

$$S_{osc}(T, B) = 2Nk_B \frac{1}{m} \sum_{j=1}^{\infty} \frac{1}{j} \cos(ju\pi) \mathcal{T}(jx) e^{-2\pi j m \gamma}. \quad (25)$$

With this result we evaluate the adiabatic temperature change in the same way as it was done in the last section, obtaining

$$\Delta T = -6T_B \sum_{j=1}^{\infty} \cos(ju\pi) \frac{L(jx_B)}{\sinh(jx_B)} e^{-2\pi j m \gamma}. \quad (26)$$

As before, we are dealing with a self-consistent problem, which we solved numerically. The calculated temperature change is presented in Fig. 3, where we can see that scattering significantly reduces the temperature change. Thus, considering a stronger scattering, i.e., increasing the scattering rate, stronger magnetic fields must be applied at lower temperatures in order to produce the same temperature change.

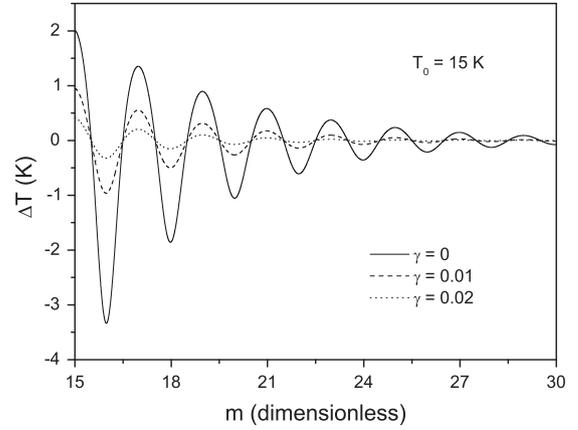


Fig. 3. Oscillating adiabatic temperature change in graphene considering the effect of scattering of electrons by defects.

### 4. Comparison with a 2D non-relativistic material

Now we turn our attention to 2D materials with non-relativistic character. Such a system consists of a thin film of diamagnetic material, previously studied considering the magnetic entropy change [8]. The magnetic entropy of this system is

$$S_{osc}(T, B) = 2Nk_B \frac{1}{n_j} \sum_{j=1}^{\infty} \frac{(-1)^j}{j} \cos(jn\pi) \mathcal{T}(jy), \quad (27)$$

where

$$n = \frac{\varepsilon_F}{\mu_B B}, \quad (28)$$

$$y = \pi^2 \frac{k_B T}{\mu_B B}, \quad (29)$$

and  $\mathcal{T}(y)$  is given by Eq. (5). Note that the entropy for both relativistic and non-relativistic systems has the same thermal dependence.

In a gas of non-relativistic electrons the dispersion relation is

$$\varepsilon = \frac{\hbar^2 k^2}{2m_e}, \quad (30)$$

as opposed to Eq. (11) that holds for relativistic electrons in graphene. Above,  $m_e$  is the electron mass. Following the same procedure employed in Section 2 for graphenes, we use the density of states

$$g_0 = \frac{m_e}{2\pi\hbar^2}, \quad (31)$$

to obtain the zero-field grand potential for the electron gas

$$\Phi_0(T) = \frac{m_e k_B^2 T^2}{2\pi\hbar^2} \text{Li}_2(-z). \quad (32)$$

Considering again Eq. (14), we obtain the grand potential at low temperatures (compared to the Fermi energy,  $k_B T \ll \varepsilon_F$ )

$$\Phi_0(T) = -\frac{m_e}{12\pi\hbar^2} (3\mu^2 + \pi^2 k_B^2 T^2). \quad (33)$$

From the above expression for the grand potential, we obtain the density of charge carriers ( $\mu \approx \varepsilon_F$ )

$$N = \frac{m_e \varepsilon_F}{2\pi\hbar^2}, \quad (34)$$

and the zero-field entropy of the system

$$S_0(T) = \frac{\pi^2 N k_B^2 T}{3\varepsilon_F}. \quad (35)$$

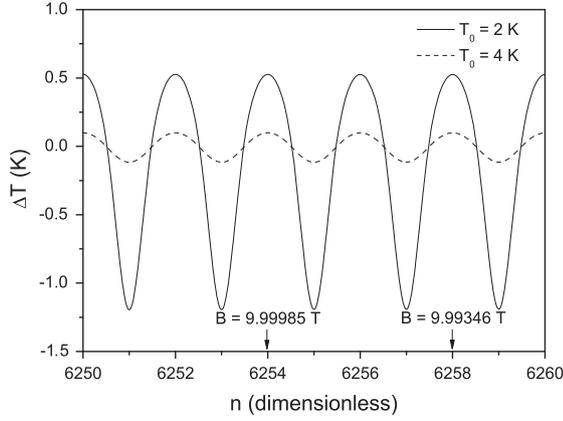


Fig. 4. Adiabatic temperature change in a 2D non-relativistic material as a function of  $n$ .

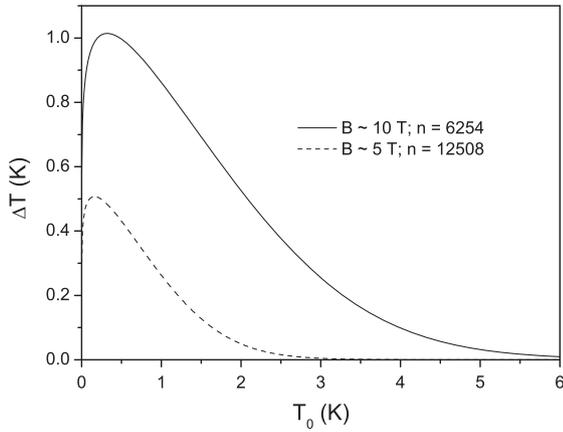


Fig. 5. Adiabatic temperature change in a 2D non-relativistic material as a function of  $T_0$ .

Note that we found an expression very similar to the one for graphene (Eq. (19)) despite the difference between the two dispersion relations, and the physics behind it. From the point of view of statistical mechanics, temperature is taken into account through Eq. (9), and enters the same way irrespective of which dispersion relation is considered.

Once we know the total entropy of the system, we apply the adiabatic condition, Eq. (20), to obtain the adiabatic temperature change

$$\Delta T = -6T_B \sum_{j=1}^{\infty} (-1)^j \cos(jn\pi) \frac{L(jy_B)}{\sinh(jy_B)}, \quad (36)$$

with  $y_B = y(T_B)$ .

Fig. 4 presents the adiabatic temperature change as a function of the inverse of the magnetic field. We see the same oscillating behavior observed earlier for graphenes. Considering a gold thin film, whose Fermi energy is  $\epsilon_F = 3.62$  eV,  $B(n=1) = 6.2539 \times 10^4$  T. On the other hand,  $B(n=10^4) = 6.2539$  T, therefore this is the order of magnitude of  $n$  corresponding to laboratory fields. Within the range of  $n$  shown in Fig. 4, the field difference between two adjacent maxima is 3.2 mT.

Fig. 5 presents the adiabatic temperature change for a gold thin film as a function of the initial temperature. Note that the maximum temperature change is lower than that observed for graphene and occurs in a lower initial temperature, despite the larger magnetic field applied.

### 5. Comparison with a 3D non-relativistic material

The first diamagnetic material to have its magnetocaloric properties investigated was a 3D non-relativistic material [5,6]. Let us briefly review its properties in order to compare with the results of the present paper. The magnetic entropy of such system is

$$S_{osc}(T, B) = \frac{3}{2} Nk_B \frac{1}{n^{3/2}} \sum_{j=1}^{\infty} \frac{(-1)^j}{j^{3/2}} \cos\left(jn\pi - \frac{\pi}{4}\right) \mathcal{T}(jy), \quad (37)$$

where  $n$  and  $y$  are given by Eqs. (28) and (29), respectively. Note that the similarity of Eqs. (3), (27) and (37), which represent, respectively, the magnetic entropy of graphene, a 2D and a 3D non-relativistic material. Following the same basic steps presented here, the temperature change for this system was found to be

$$\Delta T = -\frac{3T_B}{\sqrt{n}} \sum_{j=1}^{\infty} \frac{(-1)^j}{\sqrt{j}} \cos\left(jn\pi - \frac{\pi}{4}\right) \frac{L(jy_B)}{\sinh(jy_B)}. \quad (38)$$

Fig. 6 shows the oscillating adiabatic temperature change in a 3D diamagnetic material. Let us consider gold in bulk, whose Fermi energy is  $\epsilon_F = 5.51$  eV. We can see that  $B(n=10^4) = 9.5$  T. The field difference between two adjacent maxima in Fig. 6 is 2.1 mT.

Fig. 7 presents the adiabatic temperature change for gold in bulk as a function of the initial temperature. The initial temperature that results in maximum temperature change for bulk gold is slightly higher than the initial temperature for gold thin films; however, the value of the temperature change is lower.

### 6. Discussion

Eqs. (3), (27) and (37) suggest that the magnetic entropy of a  $d$ -dimensional system has the general form

$$S_{osc}(T, B) \propto \sum_j (B/j)^{d/2} \cos(j\alpha/B) \mathcal{T}(j\beta T/B), \quad (39)$$

irrespective of being a relativistic material by nature (graphene) or not. Above  $\alpha$  and  $\beta$  are parameters that depend on the system. From Eqs. (19) and (35), the zero-field entropy is always linear with temperature, considering the low temperature regime. We can determine the general dependence of the adiabatic temperature change with the dimension of the system applying the adiabatic condition (Eq. (20)), and the result we find is

$$\Delta T \propto -T_B \sum_j (B/j)^{(d/2)-1} \cos(j\alpha/B) \frac{L(j\beta T_B/B)}{\sinh(j\beta T_B/B)}. \quad (40)$$

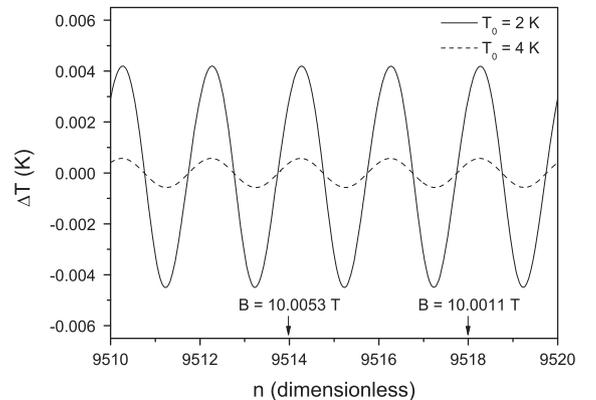


Fig. 6. Adiabatic temperature change in a 3D non-relativistic material as a function of  $n$ .

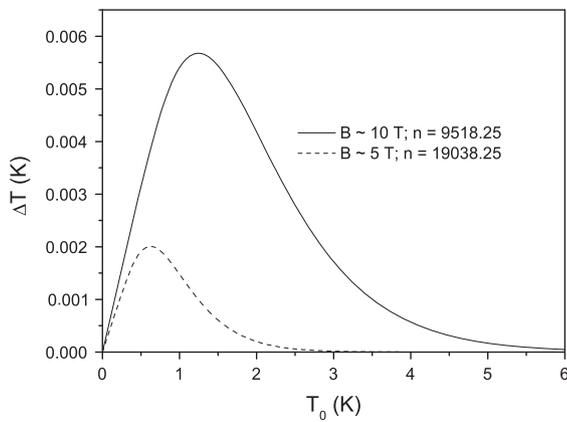


Fig. 7. Adiabatic temperature change in a 3D non-relativistic material as a function of  $T_0$ .

Thus, the general magnetic dependence of the entropy is responsible for the oscillating behavior found in magnetocaloric properties of 2D and 3D diamagnetic materials. We must emphasize the interesting fact that the adiabatic temperature change for graphene has the same magnetic and thermal dependence observed for the 2D non-relativistic electron gas.

As can be seen in Figs. 5 and 7, the temperature of maximum  $\Delta T$  for gold, film and bulk, is about 1 K (such temperature is slightly larger for bulk). With an applied field of 10 T, the temperature change of a gold film reaches 1 K, while for bulk gold it is smaller than 6 mK. For graphene, the temperature change reaches 4 K with an applied field of  $\sim 1$  T (see Fig. 2). Also, the effect is still comfortably observable at temperatures 10 times larger than those for gold (film and bulk).

It was proposed before, the use of diamagnets in bulk as field sensors [6] since they are sensitive to small field changes with a background field of the order of  $10^4$  times larger. However, 2D diamagnets would fit better to such application since they produce larger temperature changes, which can be measured easier. On the other hand, graphene would be less sensitive as a field sensor, since its period of oscillations in  $\Delta T$  is larger, but could work at higher temperatures.

## 7. Conclusion

In this paper we used a non-interacting electron gas to evaluate the adiabatic temperature change of two-dimensional diamagnetic materials. We considered two systems, namely a relativistic material, graphene, and a non-relativistic one, consisting of a thin film of diamagnetic material; and compared them with a 3D diamagnet. The adiabatic temperature change of all systems presents the same magnetic and thermal dependence. The relativistic nature of electrons in graphene, which is governed by the Dirac equation, does not produce additional effects. For the case of graphene, we also considered the effect of scattering from impurity, which strongly reduces the temperature change. At the same conditions of temperature and field, a gold film exhibits a larger temperature change than bulk gold. On the other hand, graphene exhibits even larger temperature changes at higher temperatures and smaller fields.

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