Phonon-assisted radiofrequency absorption by gold nanoparticles resulting in hyperthermia

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It is suggested that in gold nanoparticles (GNPs) of about 5 nm sizes used in the radiofrequency (RF) hyperthermia, an absorption of the RF photon by the Fermi electron occurs with involvement of the longitudinal acoustic vibrational mode (LAVM), the dominating one in the distribution of vibrational density of states (VDOS). This physical mechanism helps to explain two observed phenomena: the size dependence of the heating rate (HR) in GNPs and reduced heat production in aggregated GNPs. The argumentation proceeds within the one-electron approximation, taking into account the discretenesses of energies and momenta of both electrons and LAVMs. The heating of GNPs is thought to consist of two consecutive processes: first, the Fermi electron absorbs simultaneously the RF photon and the LAVM available in the GNP; hereafter the excited electron gets relaxed within the GNP’s boundary, exciting a LAVM with the energy higher than that of the previously absorbed LAVM. GNPs containing the Ta and/or Fe impurities are proposed for the RF hyperthermia as promising heaters with enhanced HRs, and GNPs with rare-earth impurity atoms are also brought into consideration. It is shown why the maximum HR values should be expected in GNPs with about 5 – 7 nm size.

The authors dedicate this work to the 90th anniversary of professor Leonid V. Tuzov of the Kyrgyz State University

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I. INTRODUCTION

Among methods allowing for hyperthermia in biological tissues, that based on the radiofrequency (RF) absorption by gold nanoparticles (GNPs) got in the last years much attention, due to its important advantage – a deep penetration of the RF radiation into biological tissue (∼30 cm at frequencies ∼10 MHz). Details and useful references can be found in the review by Corr et al. (2012b). Moran et al. (2009) in their experiments carried out at 13.56 MHz revealed that the heating rate (HR) depends on the particle size, namely that smaller particles are heated faster, presumably because of their higher resistivity. However, the exact physical basis of heat generation by nanoparticles remained so far unclarified. This is a serious obstacle for grasping the HR / particle size relation and hence for making “intelligent choice” of the GNP size, tailored to the particular use. For example, one may wish to assure an enhanced specific absorption rate (SAR) to heat the GNP to necessary temperatures at minimum released power, avoiding at the same time an unnecessary heating of normal tissues during hyperthermia.

According to standard definition, SAR = \( C(\Delta T/\Delta t) \), where \( C \) is the specific heat and \( \Delta T/\Delta t \) is the HR (temperature / time). The size dependence of the HR for the GNPs used by Moran et al. (2009) is presented in Fig. 1. As is seen, the HR attains maximal values, among the nanoparticles studied, in the smallest ones, of the 5 nm size. Along with Moran et al. (2009), also the observations of Kruse et al. (2011); Raoof and Curley (2011) imply that the smaller the size of GNPs (for a given volume fraction of gold), the higher their HR: among experimentally studied GNPs with diverse sizes, those of ∼5 nm diameter exhibit the highest one. Corr et al. (2012a) strengthened this conclusion, having stated that the GNPs only of size 10 nm or less could be heated by the electromagnetic RF field (again, the highest experimentally observed HR corresponded to the GNPs of 5 nm diameter).

In this paper, a physical model of the size effect in heat generation and reduction of heat generation in aggregated GNPs is proposed, in which the longitudinal acoustic vibrational modes (LAVMs) play an important role. None of the theoretical models reviewed critically by Corr et al. (2012b) took these latter into account, whereas we will show that the inclusion of acoustic modes enables to explain a number of experimental results. Besides, our findings make it possible to obtain an optimal size of GNPs providing maximum SAR.

The manuscript is organised as follows. Sec. II shows that in large GNPs (of the diameter exceeding 162 nm) the heating by RF radiation is possible owing to uncertainty in the Fermi electron’s momentum; however, the use of this mechanism in hyperthermia cannot be but very limited. For practical treatment, much smaller GNPs need to be – and indeed are – used, revealing a pronounced size dependence of the heating efficiency. Possible physical foundations of the related heating mechanism, along with explanation

![FIG. 1 Size-dependent heating of gold nanoparticles (diameters indicated) in the RF field of the frequency 13.56 MHz. Reproduced with permission from Moran et al. (2009).](image-url)
of the observed size effect, are discussed in Sec. [III] on the basis of conclusions drawn from Sec. [III] the experimentally observed reduced heat production in aggregated GNPs is explained. Sec. [V] addresses possible ways of further increase of the HP in GNPs. The general discussion of results is offered in Sec. [VI] and the conclusion drawn in Sec. [VII].

II. SETTING THE STAGE; CONDITIONS FOR THE RF ABSORPTION

First we discuss an issue of whether the phonons are at all needed for the RF absorption, and what are the conditions for the latter to happen in a “conventional” way. The key feature in absorption of electromagnetic waves by nanoparticles is quantization of energy levels, which become denser as the particle size increases. Satisfying the conditions of conservation of both energy and momentum on absorption is not, a priori, possible without additional considerations, because the curvature/slope of dispersion relations are very different for electrons and photons. We consider first the case when no other players enter the picture, and assume the matching conditions to be satisfied within the uncertainty relation. To be specific, we take the GNP to be spherical, of diameter $D$; the RF of 13.56 MHz, like in the above experiment, corresponds to photon energy $h\nu = 5.6 \times 10^{-8}$ eV and momentum $p_{\text{ph}} \approx 3 \times 10^{-30}$ g cm s$^{-1}$.

The skin depth in gold at 13.56 MHz is about 20 $\mu$m, i.e., by orders of magnitude exceeding the GNP size. One can therefore assume that the electric field penetrates the volume and is of the same strength throughout the particle.

In metal particles as small as $\sim 5$ nm, and even for much larger ones, the quantization (discreteness) of the electron energy spectrum is a crucial factor shaping their properties. Speaking specifically about gold, one can advance far enough on the basis of the free-electron model, assuming one electron per atom and estimating the corresponding Fermi energy.

Assume that the absorption happens due to transitions between discrete levels induced by quantum confinement; the free-electron dispersion relation $E = p^2/2m$ implies that the energy step $\Delta E_{\text{el}} = E_{\text{el}}'$ must be accompanied by the correction of momentum, $\Delta p_{\text{F}} \approx E_{\text{el}}'/m = h\nu/v_{\text{F}}$ (see Fig. 2). For the relevant values of $h\nu = 5.6 \times 10^{-8}$ eV and the Fermi velocity of gold as in the free-electron model ($v_{\text{F}} \approx 1.4 \times 10^6$ m s$^{-1}$), the momentum mismatch amounts to $\Delta p_{\text{F}} \approx 6.4 \times 10^{-28}$ g cm s$^{-1}$, two orders of magnitude larger than what the photon momentum (see above) could bring about. However, the small size of GNP may result in appreciable Heisenberg’s uncertainty of electron momenta in them and thus “smear out” the discussed mismatch condition. Let us make some estimates to this end.

Following the pioneering works by [Kubo, 1962, 1977], we remind a relationship between the diameter $D$ and the level spacing $\Delta E_{\text{el}}$. Assume that the electron energy level $E'$ is the first vacant one above the Fermi level $E_{\text{F}}$. The level spacing $\Delta E_{\text{el}} = E' - E_{\text{F}}$ and the number of atoms $N_a$ in the GNP are related as follows [Kubo, 1962] the derivation of the Kubo’s formula is given in Appendix A:

$$\Delta E_{\text{el}} \approx \left(\frac{4}{3}\right) \frac{E_{\text{F}}}{N_a}, \quad \text{or} \quad N_a \approx \left(\frac{4}{3}\right) \frac{E_{\text{F}}}{\Delta E_{\text{el}}};$$

$$D \approx \left(\frac{8 \ m_a \ E_{\text{F}}}{\pi \ \rho \ \Delta E_{\text{el}}} \right)^{1/3},$$

(1)

FIG. 2 Scheme of absorption of RF photon by the Fermi electron without involvement of LAVM. Dashed curve indicates a transition of the Fermi electron excited by the RF photon with energy $h\nu$. 
FIG. 3 Schemes of "direct" absorption of RF photons $h\nu$ by electrons at the Fermi level $E_F$, for different energy discretisation steps $\Delta E$, depending on the particle size, and for different step multiplicities $\alpha$ (see text and Table I for details). The uncertainty of the electron’s momentum is hinted by elliptical dots of different width.

where $m_a$ is the atomic mass of gold, $m_a = 197$ in atomic units, or $\approx 3.27\cdot10^{-22}$ g; $\rho = 19.3$ g$\cdot$cm$^{-3}$ is the density of gold, $E_F = 5.52$ eV. For $\Delta E_{el} = h\nu = 5.6\cdot10^{-5}$ meV, $D = 162.1$ nm. Remind that these are estimates for the smallest GNP size which allows the RF absorption at 13.56 MHz, from the energy level spacing arguments. Now, we turn to the momentum uncertainty arguments and assume for simplicity that the direction along the nanoparticle’s diameter is collinear with the momentum $\Delta p_F$ and the Fermi electron’s momentum $\vec{p}_F$. Then the uncertainty in the Fermi electron’s momentum in this direction equals $\Delta p \sim \hbar/(2\piD)$. At $D = 162.1$ nm, $\Delta p \sim 6.5\cdot10^{-23}$ g$\cdot$cm$\cdot$s$^{-1}$, that largely exceeds $\Delta p_F \approx 6.4\cdot10^{-28}$ g$\cdot$cm$\cdot$s$^{-1}$. Consequently, the momentum conservation law can be helped by such uncertainty, and the RF photon absorbed. We keep in mind, however, that the minimal GNP size for the direct RF absorption must be at least $\approx 162.1$ nm. Obviously as the particle size grows, the distance between quantified levels shrinks, so that an absorption of a given photon $h\nu$ may bring about an excitation across $\alpha$ (an integer number) interlevel distances. This situation is schematically shown in Fig. 3 which implies a parabolic dispersion law $E = p^2/2m$ for different confinements (particle sizes), in arbitrary scale. The effect of the momentum uncertainty is indicated by dots of different widths placed at the initial and final levels. Some numerical estimates for the energy spacings and momentum uncertainties, relevant for the absorption of quanta at $\nu = 13.56$ MHz ($h\nu = 5.6\cdot10^{-5}$ meV) are summarized in Table I. An issue of matrix elements for such transitions, some of which might be suppressed in the dipole approximation due to symmetry considerations, is left aside. The numerical relation between the energy split multiplicity $\alpha$, given by $\Delta E_{el} = h\nu/\alpha$, and the diameter of particle (assuming the latter spherical) from Eq. (1) is as follows:

$$D \approx \alpha^{1/3}\cdot[(8/\pi)\cdot(m_a/\rho)\cdot(E_F/h\nu)]^{1/3} = \alpha^{1/3}\cdot 162.1 \text{ [nm]}.$$

(2)

TABLE I Parameters of GNPs with level spacings $h\nu/\alpha$ ($\alpha$=1, 2, 4, 10 taken as examples) able to absorb the 13.56 MHz photons thanks to the uncertainties in the Fermi electrons’ momenta.

| Number of level spacings $\alpha$ | Level spacing $h\nu/\alpha$ (10$^{-5}$ meV) | Diameter $D_\alpha$ (nm) | Uncertainty in Fermi electron’s momentum $\Delta p_\alpha$ (10$^{-23}$ g$\cdot$cm$\cdot$s$^{-1}$) |
|----------------------------------|---------------------------------|-----------------|---------------------------------|
| 1                                | 5.6                            | 162.1           | 6.5                             |
| 2                                | 2.8                            | 204.2           | 5.2                             |
| 4                                | 1.4                            | 257.3           | 4.1                             |
| 10                               | 0.6                            | 349.2           | 3.0                             |
The last column of Table I specifies the corresponding momentum uncertainty, \( \hbar/(2\pi D) \). In all the cases considered (until entering much larger particle sizes than those covered by Table I), the uncertainty in the Fermi electron’s momentum \( \Delta p_\text{el} \) exceeds by far the “adjustment” \( \Delta p_\text{ph} \approx 6.4 \times 10^{-28} \text{ g-cm-s}^{-1} \), discussed above as a reference value to absorb the momentum mismatch required to promote a Fermi electron onto the energy level \( (E_\text{F} + \hbar \nu) \). Thus, the momentum conservation law can be fulfilled, and the 13.56 MHz photons absorbed, for GNPs larger than \( \sim 162 \text{ nm} \). Consequently the latter, as it seems, can apparently be RF-heated “directly”, i.e., without involvement of LAVMs, just by exciting the Fermi electrons to the available energy levels above the Fermi level. On the contrary, in GNPs smaller than \( \sim 162 \text{ nm} \) the separation between adjacent levels exceeds the energy of the RF quantum, and at “working” particle sizes which in fact show an enhanced absorption (\( \sim 5 \text{ nm} \)) the level splitting becomes prohibitively large. An involvement of many photons in a single electron excitation is likely to be a very rare process. Therefore, we have to bring another physical mechanism into consideration. Longitudinal acoustic phonons seem to be able to intervene with energies of the “correct” order of magnitude. The prerequisites of their practical involvement are discussed in the following.

III. LAVM-ASSISTED ABSORPTION OF RF PHOTON BY A FERMI ELECTRON

The observed size dependence of the HR can be explained by a mechanism of the GNPs’ heating that attributes a crucial role in the absorption of a RF photon to LAVM. To make reliable estimates, we need to know something about elastic properties of nanoparticles. A theoretical work by D.Y. Sun et al. (2001) demonstrated that the metallic nanoparticles retain the bulklike core region. Experimentally, J. Sun et al. (2014) have recently found that Ag nanoparticles can be deformed like liquid droplets but remain highly crystalline in the interior.

As was already admitted above, we assume the GNP to be spherical; we remind that the RF of 13.56 MHz corresponds to photon energy \( \hbar \nu = 5.6 \times 10^{-8} \text{ eV} \) and momentum \( p_{\text{ph}} \approx 3 \times 10^{-20} \text{ g-cm-s}^{-1} \). The absorption happens due to transitions between discrete levels induced by quantum confinement, as was elaborated above and schematically shown in Fig. 3.

From now on, we turn to discussing a case of nanoparticles too small for a RF phonon energy to “bridge the gap” between largely split quantified levels. We bring into consideration a scheme of absorption of a RF photon whereby a Fermi-level electron excitation is helped by an involvement of a LAVM. A “classical” view onto the electron-phonon interaction (otherwise straightforwardly grasped in terms of energy and momentum exchange between the corresponding quasiparticles) is that the electrons are driven by, or themselves contribute to, the fluctuating electric field due to compression / dilation of the electron density in the course of lattice vibrations. Obviously, only the longitudinal vibration mode can be “useful” in this sense. Its wavevector moreover must be reasonably far from the Brillouin zone (BZ) center, where the dispersion starts to bend “flat” and to yield high density of modes.

A Fermi electron may absorb the energies of both the RF photon and the LAVM. Fig. 4 shows how an inclusion of momentum \( n_{\text{vm}} \vec{q} \) and energy \( n_{\text{vm}} \Delta E_{\text{vm}} \) of such LAVM (\( n_{\text{vm}} \) numbers the energy steps in the vibration modes) into the combined absorption makes possible to satisfy both conservation laws. In the absorption event, the GNP borrows energy from its LAVMs system, adds it to that of the RF quantum and excites an electron to the vacant level beyond the \( E_\text{F} \):

\[
E_\text{F} + \Delta E_{\text{vm}} + \hbar \nu = \left( \vec{p}_\text{F} + \vec{q} + \vec{p}_{\text{ph}} \right)^2 / 2m ,
\]

where \( E_\text{F}/\vec{p}_\text{F} \), \( \Delta E_{\text{vm}}/\vec{q} \) and \( \hbar \nu/\vec{p}_{\text{ph}} \) are the energy / momentum of the free electron, the LAVM and photon, correspondingly (see Fig. 4), and \( m \) is the electron’s mass. We note, for the sake of a later reference, that an electron may well be excited across \( m_{\text{el}} > 1 \) steps of its discrete spectrum, i.e., onto \( E_\text{F} + m_{\text{el}} \Delta E_{\text{el}} \), that is however not explicitly depicted in Fig. 4. Once excited, the propagating mobile electron very likely will be trapped (relaxed) before reaching the GNP surface (see Subsec. II.C on the mean free path issues), releasing more energy to the LAVMs pool than was borrowed beforehand. The net effect of that is the heating of the GNP.

\(^{1}\)A numerical estimate can be drawn from Singh and Ali (2013), who studied the phonon dispersions in amorphous metals. For gold, the first maximum of the \( \omega(\vec{q}) \) dispersion occurs at \( q \sim 1.5 \text{ Å}^{-1} \) whereas up to \( q \sim 1.0 \text{ Å}^{-1} \) the dispersion remains reasonably linear.
In Fig. 4 a point on the Fermi sphere (identified by momentum $\vec{p}_F$ and energy $E_F$) serves as an origin of the LAVM dispersion branch, on which the momentum $n_{vm} \vec{q}$ and the mode energy $\Delta E_{vm}$ stand for some “representative” mode. Let us give some numerical estimates to these parameters.

The free-electron model for bulk gold yields the Fermi radius $k_F = 1.20 \times 10^{10} \text{ m}^{-1}$, quite close to the mean experimental estimates for its slightly non-spherical belly [Coleridge and Templeton 1982]. The corresponding free-electron Fermi energy is $E_F = 5.52 \text{ eV}$; the Kubo formula for the level splitting at the Fermi energy due to spatial confinement $\Delta E_{vm}$ yields, for the diameter $D = 5 \text{ nm}$, $\Delta E_{vm} = 1.91 \text{ meV}$, and the corresponding increment of the electron’s momentum to bring it to the first vacant level is $\Delta k_F = 2.08 \times 10^6 \text{ m}^{-1} \approx 0.017$ of the $k_F$. As RF $h \nu = 5.6 \times 10^{-5} \text{ meV} \ll \Delta E_{vm}$, the larger part of the latter gap has to be overcome, according to our hypothesis, by borrowing energy from LAVM. From the velocity of sound in gold ($3240 \text{ m} \cdot \text{s}^{-1}$ longitudinal, $1200 \text{ m} \cdot \text{s}^{-1}$ transversal), the highest phonon energy extrapolated onto the nearest BZ boundary, i.e., the L point, is $\sim 28.5 \text{ meV}$ ($L_1$) and $\sim 10.5 \text{ meV}$ ($L_T$). Corresponding experimental frequencies at $L$ are bended downwards as expected, to, correspondingly, 19.1 and 7.7 meV [Dal Corso 2013, see also his first-principles calculation of vibration spectrum]. Consequently, the energy matching to $\Delta E_{vm}$ can be realized via an interaction with an acoustic phonon whose momentum is within $\sim 7 - 18\%$ of the BZ radius. Inversely, an interaction with a phonon close to the BZ periphery may, in principle, promote an electron onto a higher (up to the 3rd or 4th) energy state beyond the Fermi level. Two observations, however, need to be stressed in this relation. First, the numerical relations in gold (see above) are such that matching the energies of electron and phonon is impossible if their momenta stay collinear, as Fig. 4 implies. A more realistic scenario, discussed below, comprises $k_F$ staying at some angle to the phonon momentum $\vec{q}$. The second observation imposes the quantisation of phonon $\vec{q}$ values in a nanoparticle as $q = h / L$, where $L$ is a length of the chain of ions along which the LAVM propagates. As an estimate of the order of magnitude, the relevant length is between the nanoparticle’s diameter (5 nm) and circumference, hence the $q$ step is $\Delta q = [1 \cdot 2\pi] / L = [0.2 \cdot 1.26] \times 10^6 \text{ m}^{-1}$, i.e., $\sim 2 - 11\%$ of $k_F$.

In the following, we’ll often refer to circular contour / path over which the compression mode propagates, as this is a simple yet realistic model case. Although the natural diversity of nanoparticle sizes and shapes makes a faithful simulation difficult, the circular path has a virtue of being the longest one in a “round” particle, hence hosting the maximal number of modes, densely distributed in the $\vec{q}$ space. Consequently, the quantified energies of modes on a circular contour make a denser spectrum than those on any other path: within a given energy interval, more individual modes can be found and used for borrowing energy to an electron. It will be argued below that longitudinal acoustic phonon cannot propagate strictly on the surface, but rather at a (small) depth.

We discuss now the impact of the electron and phonon momenta being non-collinear, but, in any case, coplanar. A more realistic scheme in this sense than that of Fig. 4 is shown in Fig. 5, where however the energy and the momentum of the RF photon are neglected, by force of relations $h \nu \ll E_{vm}$; $p_{ph} \ll n_{vm} q$; $p_{ph} \ll p_F$. Fig. 5 depicts therefore a possibility of absorption, by electrons at the Fermi surface, of the LAVMs with energies $\Delta E_{vm}$, $2 \Delta E_{vm}$, $3 \Delta E_{vm}$, and corresponding momenta, within the same nanoparticle of a given size. It is (arbitrarily, just for the sake of simplifying the figure) implied that $m_{el} = n_{vm}$ and hence $\Delta E_{el} = \Delta E_{vm}$, therefore the augmentation of the electron energy on absorption happens in portions of $\Delta E_{vm}$.
FIG. 5 Same as in Fig. 4 however assuming $m_{cl} = n_{vm}$ and $\Delta E_{el} = \Delta E_{vm}$, for the general case of the electron momentum $\vec{p}_F$ and the phonon momentum $\vec{q}$ being coplanar. For simplicity, the energy and the momentum of the RF photon are neglected. See text for details.

A more detailed projection of the momenta matching, involving also the RF photon momentum, is shown in Fig. 6. Possible excitations from an initial state $\vec{p}_F$ of energy $E_F$ via an absorption of a phonon $\vec{q}$ and a RF photon $\vec{p}_{ph}$ end up in a state with the energy $E = E_F + \Delta E_{vm} + h\nu$. The allowed "chained" $\vec{p}_F \cdots \vec{q} \cdots \vec{p}_{ph}$ vectors fall within a body of revolution around the fixed $\vec{p}_{ph}||\vec{p}_x$ direction, limited on the left by the cone of [side $\vec{p}_F$ / aperture $2\beta$] and on the right – by the spherical (radius $|\vec{p}_F + \vec{q} + \vec{p}_{ph}|$) cape built on top of the cylinder of the height $p_{ph}$. The conical and cylindrical surface parts are connected by the intermediate conical belt of the width $q$. From Fig. 6(a), the maximal angle $\beta$ the $\vec{p}_F$ vector may build to $\vec{q}$ is

$$
\beta = \arccos \left( \frac{\sqrt{2m_eE - q^2} - p_{ph}^2 - p_F^2(\vec{p}_{ph} \cdot \vec{p}_F)}{2(p_{ph} \cdot \vec{p}_F)} \right). 
$$

On relaxation of the excited electron back to $E_F$, the extra energy $E' = \Delta E_{vm} + h\nu$ is released into the vibration pool, exciting a phonon with $|\vec{q}'| > |\vec{q}|$. $h\nu$ is therefore the net gain in energy.

FIG. 6 Projection of the vector construction from Fig. 5 onto the plane comprising the $\vec{p}_F$ and $\vec{q}$ vectors; the photon momentum $\vec{p}_{ph}$, neglected in Fig. 5, is now retained. Circles centered at the origin of the coordinate system, of radii $|\vec{p}_F|$ and $|\vec{p}_F + \vec{q} + \vec{p}_{ph}|$, are cross-sections of the electron energy paraboloid at $E = E_F$ and $E = E_F + \Delta E_{vm} + h\nu$. (a): Some examples of matching momenta and energies in the process of electron excitation from $\vec{p}_F$ due to absorption of phonon $\vec{q}$ and RF photon $\vec{p}_{ph}$. (b): For one of $\vec{p}_F$ vectors from panel (a), excitation channels are followed by possible relaxation channels into the initial state via release of phonon $\vec{q}'$. Note that $|\vec{q}'| > |\vec{q}|$. 
In the following, we consider the LAVM within a GNP as a compression wave propagating along a closed chain of atoms, in the spirit of the Born – von Kármán cyclic boundary conditions. For this analysis, the work by D.Y. (Sun et al., 2001) is useful which deals with elastic properties and vibrational density of states (VDOS) in GNPs, indicating notably three structure elements of a nanoparticle: the surface shell (of ≈ 2 Å thickness), the transition shell (of ≈ 3 Å thickness beneath) and the core region. Fig. 7 depicts the corresponding decomposition of VDOS for the case of 959-atom GNP, of the diameter ≈ 3.2 nm. In the core and transition shell, the distribution of VDOS clearly shows the peaks at ≈ 3.7 THz (E_{vm} ≈ 15.3 meV), resembling the peak in the VDOS of bulk gold in the experimental work by (Muñoz et al., 2013), which we attribute as being due to LAVMs (see Fig. 8). The VDOS of the surface shell in Fig. 7 does also indicate a feature at the corresponding energy, that we extracted from the background as the curve 4 in Fig. 7.

The VDOS maximum under discussion is strongest in the core region, which is therefore expected to contribute mostly to the RF absorption. According to D.Y. (Sun et al., 2001), the core region is bulklike, therefore while discussing its contribution to the RF absorption, one can rely on the density and sound velocity values for crystalline gold. This is consistent with experimental observations on the gold’s homologue, silver, by J. (Sun et al., 2014) who have found that its nanoparticles remain highly crystalline in the interior. In the following discussion, we assume that the “useful” LAVMs propagate at the depth δ = 0.7 nm, i.e., along the closed contour entirely within the bulklike core region.

FIG. 7 VDOS in Au_{959} nanocrystal, reproduced with our modification with permission from (Sun et al., 2001). Curve 1: contribution from the surface shell; curve 2: from the transition shell, curve 3: from the core region; curve 4: our approximate extraction of the VDOS for LAVMs in the core region, yielding a peak centered at 3.7 THz (15.3 meV), with full width at half maximum (FWHM) ∼1 THz (∼4.14 meV).

FIG. 8 Experimental phonon DOS curves for bulk pure Au and Au_{0.97}Fe_{0.03} from the inelastic neutron scattering measurements; reproduced with permission from (Muñoz et al., 2013). Dashed line is our approximate extraction of the VDOS curve for LAVMs (the FWHM range is from 14.6 to 18.4 meV; the peak position is at 16.8 meV).
A. Energy conservation

We discuss now some quantization relations for electrons and LAVMs following from the GNP geometry. The energy conservation condition for the absorption of a RF photon with the energy $h\nu$ is as follows:

\[ m_{el} \Delta E_{el} = n_{vm} \Delta E_{vm} + h\nu \approx n_{vm} \Delta E_{vm} . \tag{5} \]

Here, $m_{el}$ is the number of steps (gaps) between the quantized electron levels, and $n_{vm}$ the number of vibration quanta helping a RF photon to get absorbed. According to the Kubo’s formula (Kubo, 1962, 1977) – see also Eq. (A4) in the Appendix A – the step in the electron energy levels $\Delta E_{el}$ depends on the number of gold atoms $N_a$. The condition (Eq. 5) that $m_{el}$ energy steps must embrace $n_{vm}$ phonon energies takes the form

\[ \frac{4}{3} m_{el} \frac{E_F}{N_a} \approx \frac{n_{vm} v_L h}{\pi(D - 2\delta)} , \tag{6} \]

where $L = \pi(D - 2\delta)$ is the length of the closed contour at the depth $\delta$ under the GNP surface, and the (longitudinal) sound velocity $v_L$ relates frequency to wave vector. Further on, assuming that the density of gold in the surface shell and the transition shell is close to that in the core region, i.e. in bulk gold, the number of atoms in GNP can be expressed via density of gold $\rho$, atomic mass $m_a$ and the volume $V$ (or diameter $D$) of the particle:

\[ N_a \approx \frac{\rho V}{m_a} = \frac{\pi}{6} \frac{\rho}{m_a} D^3 . \tag{7} \]

Taken together with Eq. (6), this yields the depressed cubic equation on $D$:

\[ D^3 + p D + q = 0 , \tag{8} \]

with

\[ p = -\frac{8 E_F m_a}{v_L h \rho} \left( \frac{m_{el}}{n_{vm}} \right) ; \quad q = \frac{16 E_F m_a \delta}{v_L h \rho} \left( \frac{m_{el}}{n_{vm}} \right) . \tag{9} \]

For $p < 0$ and $q > 0$, Eq. (8) always has one negative root and either two (possibly degenerate) or none positive ones. The two positive roots of Eq. (8) can be expressed as follows:

\[ D_k = -2 \sqrt{\frac{|p|}{3}} \cos \left\{ \frac{1}{3} \arccos \left[ \frac{q}{2 \sqrt{|p|}} \right] \right\} + \frac{2\pi k}{3} \}, \tag{10} \]

where $k = 1, 2$. Note that the parameters $p$ and $q$ contain, along with constants depending on the properties of gold, the trial numbers $\delta$, $m_{el}$ and $n_{vm}$; recall that $\delta$ is the depth of propagation of LAVM, and $n_{vm}$ is the number of vibration quanta matching within the electronic excitation. The solutions $D_k$ can be expressed in terms of $\delta$, $m_{el}$ and $n_{vm}$ as follows ($D_k$ and $\delta$ measured in nm):

\[ D_k = -8.64 \sqrt{\frac{m_{el}}{n_{vm}}} \cos \left\{ \frac{1}{3} \arccos \left[ 0.695 \delta \sqrt{\frac{n_{vm}}{m_{el}}} \right] \right\} + \frac{2\pi k}{3} \}, \tag{11} \]

Of two positive roots given by Eq. (11), we retain the practically relevant largest value of $D_k$, corresponding to $k = 1$. Note that certain combinations ($m_{el}$, $n_{vm}$) yield the argument of arccosine $> 1$ and hence no solution. The roots are densely yet unevenly distributed, as is shown by Fig. 3. Note that the total number of solutions increases, as expected, with the number of trial ($m_{el}$, $n_{vm}$) combinations, however the profile of the root density, with its narrow maximum around $\approx 7$ nm, remains stable up to the upper $\approx 25\%$ of the total span of $D$ values. For this reason, and moreover since a non-ideal equidistanteness of both electrons’ and LAVMs’ levels would eventually “detune” the criteria set by Eqs. (5, 6) for large ($m_{el}$, $n_{vm}$), we set, from now on, an arbitrary limit ($= 10$) on the maximal values of the latter.

We’ll see below that this remarkable “selectivity” of GNP sizes $D$ with respect to their capacity to satisfy the energy conservation relations will eventually manifest itself in the distribution of the HR. The latter
ought to be influenced, however, by the next element entering our discussion, namely, the availability of “useful” LAVMs that can be induced in the particles of selected sizes. “Useful” means the modes whose energies are multiples of \( n_{vm} \cdot \Delta E_{vm} = n_{vm} \cdot v_L h / [\pi (D - 2\delta)] \), \( n_{vm} \) being selected by the commensurability of the vibration energies with electron excitation ones, in the spirit of Eq. (5). Obviously, for the optimal heating it is essential to find many such vibrational modes within the FWHM of the LAVM-related VDOS peak of gold (cf. Figs. 7,8 and the related discussion), the number we’ll refer to as \( N_{FWHM} \) in the following.

B. Momentum conservation

In addition to the energy conservation equation (5), one should take into account the momentum conservation condition. We’ll specify it for the case of LAVM propagating along the circular contour of the diameter \( D - 2\delta \), to which the phonon momentum \( n_{vm} \vec{q} \) is tangential – see Fig. 10. Anywhere on the contour, a Fermi electron with the momentum \( \vec{p}_F \) can intervene to bring about an absorption of a RF photon (we neglect the effect of the momentum and energy of the latter onto the resulting conservation relation, as was already argued before).

The situation arbitrarily shown in Fig. 10 assumes the momentum of the Fermi electron to point inwards the GNP; on absorbing a phonon, such electron would transverse the particle along the path \( l \) and release the phonon “on the other side” of the contour. A different possibility would be the \( \vec{p}_F \) pointing outwards; on the nanoparticle’s surface such electron would be either elastically reflected inwards, or emit a quantum and be “lost” for the GNP heating mechanism we discuss. The probability relation for such elastic / inelastic

![FIG. 10 Scheme of RF photon absorption on a circular contour inside a nanoparticle; see text for discussion.](image)
events at the surface is a priori difficult to estimate. Anyway, the elastically scattered electron will almost “instantly” regain the contour and follow the path of the inwards-moving electron, as depicted in Fig. 10. To specify what “instantly” means, we note that the perturbation of the potential inside the particle, “felt” by an electron, propagates, at most, with the longitudinal sound velocity in gold, i.e., $v_L = 3.23 \times 10^5 \text{ cm s}^{-1}$, whereas the Fermi velocity in gold is three orders of magnitude larger: the free-electron model with the electron density corresponding to that of monovalent gold yields $v_F = 1.4 \times 10^8 \text{ cm s}^{-1}$ (cf. Sec. 11 see also Ashcroft and Mermin [1976]). The “flight time” for the electron to reach the surface of the nanoparticle and get back to the contour is therefore $\sim 10^{-15} \text{ s}$.

A simple geometric argument illustrated by Fig. 10 (for the ideal case of planar circular contour) shows that the momentum of the absorbed phonon $n_{vmq}$ can “ride” the electron across the particle and be released on the other side of the contour, that we’ll refer to as relaxation. In fact, simultaneously released are the Fermi momentum $\vec{p}_F$ and the phonon momentum $n_{vmq}$, both at angles with their respective “pre-absorption” values but exactly preserving the corresponding moduli, under the condition that the phonon is emitted along the contour at the electron’s contact with the latter on arrival. Specifically in Fig. 10, the transferred momentum $\vec{s}$, a sum of the electron $\vec{p}_F$ and phonon $n_{vmq}$ momenta are related to the electron emission angle $\gamma$ as follows:

$$ p_F^2 = s^2 + (n_{vmq})^2 - 2s(n_{vmq}) \cos \gamma, \quad (12) $$

i.e., the angle the momentum of the excited electron makes to the contour is

$$ \gamma = \arccos \frac{s^2 + (n_{vmq})^2 - p_F^2}{2s(n_{vmq})}. \quad (13) $$

Fig. 10 implies moreover that the momentum of a LAVM phonon, via the interaction with an electron, may be “reinforced” by that of RF photon. The “parallel” (along the contour) component of the latter is then added to $n_{vmq}$ and transferred (by mediation of the excited electron) to the relaxation point. The momentum of then released phonon is $n_{vmq}$, with $|\vec{q}| > |\vec{q}|$, even if the net increase of the phonon momentum is quite small, with respect to electron and phonon counterparts: $h\nu \ll \Delta E_{vm}; p_{ph} \ll nq, p_{ph} \ll p_F$.

The magnitude of $s$ in Eq. (13) is $s = \sqrt{2m(E_F + n_{vmq}\Delta E_{vm})}$. On expressing the magnitude of the LAVM momentum $q$ and the energy step via the nanoparticle size $D$ and the velocity of (longitudinal) sound $v_L$,

$$ q = h/[\pi(D - 2\delta)]; \quad \Delta E_{vm} = v_Lh/[\pi(D - 2\delta)], \quad (14) $$

we arrive at an expression for $\gamma$ in terms of $n_{vm}$ and $(D - 2\delta)$:

$$ \gamma = \arccos \left\{ \left[ m v_L + \frac{n_{vm}h}{2\pi(D - 2\delta)} \right] \left[ p_F^2 + \frac{2m n_{vm}v_Lh}{\pi(D - 2\delta)} \right]^{\frac{1}{2}} \right\}. \quad (15) $$

An excited electron would traverse the nanoparticle (along the chord $l$ in Fig. 10) and release energy on entering the cyclic contour again, whereby a vibration mode with momentum $n_{vmq}$ would be induced. Technically this might happen as a consequence of an electric field being suddenly created at the “arrival point” of the electron on the contour; the Coulombic attraction of the ions would trigger the compression wave to run along the contour. The electron path (chord) is related to the nanoparticle parameters $n_{vm}, D, \delta$ as follows:

$$ l = (D - 2\delta) \cos \left( \frac{\pi}{2} - \gamma \right) $$$$ l = (D - 2\delta) \sin \arccos \left\{ \left[ m v_L + \frac{n_{vm}h}{2\pi(D - 2\delta)} \right] \left[ p_F^2 + \frac{2m n_{vm}v_Lh}{\pi(D - 2\delta)} \right]^{\frac{1}{2}} \right\}. \quad (16) $$

For relevant values of $n_{vm}$ and $(D - 2\delta)$, the argument of arccosine varies within $\sim 0.006 - 0.187$. Consequently the sine in the above formula stays within 0.982 - 0.999, i.e., $l \approx (D - 2\delta)$ with, at most, $\approx 2\%$ accuracy, therefore the excited electron must transverse the nanoparticle roughly along the latter’s axis. On neglecting the discreteness on the circle of LAVM propagation (of the $D - 2\delta$ diameter), each its point may serve as the “source” of the excited electron. The regions of absorption of RF photons in the nanoparticle are the rings of $(D - 2\delta)$ diameter.
C. Electron free path

The probability for an electron to transverse the particle, i.e., to escape being scattered along the path of the length \( l \) and to reach the “opposite” point on the cyclic contour, equals \( \exp\left(-l/l_0\right) \approx \exp\left[-(D - 2\delta)/l_0\right] \), where \( l_0 \) is the mean free path of an electron in the nanoparticle of the size \( D \) (see below).

It seems logical that the HR of a nanoparticle of size \( D \) is proportional to the following factors: (i) the energy of absorbed RF photons, (ii) the length of the contour \( \pi(D - 2\delta) \) (as the absorption may occur in any point thereupon); (iii) the summary number \( \sum_i N_{\text{FWHM}}^{(i)} \) of matching opportunities for the multiple energy step \( n_{\text{vm}} \Delta E_{\text{vm}} \) to fall within the energy range of FWHM vibration modes [the estimates are 14.60 – 18.40 meV according to \( \text{Muñoz et al. } 2013 \), or 12.86 – 16.54 meV according to D.Y. \( \text{Sun et al. } 2001 \)], and (iv) the probability for an excited electron to undergo relaxation on the contour, i.e., \( \exp\left[-(D - 2\delta)/l_0\right] \).

\[
HR \sim h\nu \cdot 2\pi (D - 2\delta) \sum_i N_{\text{FWHM}}^{(i)} \exp\left[-(D - 2\delta)/l_0\right].
\]

Here, the factor 2 accounts for two senses of propagation of vibration modes along the closed contour, and the index \( i \), without further elaborating for the moment, identifies absorption / relaxation “events” likely to contribute to the HR. This summation should, at least, take into account different combinations \( (m_{\text{el}}, n_{\text{vm}}) \), within the global limitation \( \leq l_0 \) imposed on these parameters, which retain \( n_{\text{el}}/n_{\text{vm}} \) and thus correspond to the same solution \( D \) of Eq. (11), but whose values \( N_{\text{FWHM}} \) are different. In the next subsection, we’ll adress an issue of multiple contours which may participate in the absorption and the relaxation events, in which relation the summation will be further explained. For the time being, we retain the general structure of the expected expression for the HR, and try to specify the relevant value of \( l_0 \). The upper limit on it is the mean free path in bulk gold, \( \approx 35 \text{ nm} \); in nanoparticles, due to irregularities of internal structure, \( l_0 \) ought to be much shorter. A priori, the smaller the size, the more likely the crystal lattice is distorted, hence the smaller the mean free path. Estimates for some “working” value for small enough GNP sizes, which were covered by the study by \( \text{Moran et al. } 2009 \), can be gained from their experimental data reproduced in Fig. 4 with the help of insight given by Eq. (17).

Fig. 4 reveals a tendency towards the “saturation” of curves with an increase of the gold volume fraction. This reflects the loss of efficiency of heating the nanoparticles following their aggregation: the higher the GNP concentration, the higher the probability of their agglutination. Therefore the “net” \( l_0 \) values are more safely to extract from the slope of curves \( d(\text{HR})/d(\text{volume fraction}) \) near the origin. Of interest for us is the value of \( l_0 \) for GNP’s with \( D_1 = 5 \text{ nm} \) and \( D_2 = 10 \text{ nm} \); the corresponding slopes are almost identical. Eq. (17) yields the following relation for the curves corresponding to these values of \( D \):

\[
\frac{HR_2}{HR_1} \approx \frac{D_2 - 2\delta}{D_1 - 2\delta} \frac{D_2}{D_1} \sum_i \left[ N_{\text{FWHM}}^{(2)} \right] \exp\left(\frac{D_1 - D_2}{l_0}\right).
\]

As mentioned above, each sum implies all relevant absorption / relaxation events within the particle of the corresponding size. Practical calculations show that, in order to estimate the \( HR_2/HR_1 \) ratio from the data of Fig. 4 with the accuracy of \( \approx 10\% \), it suffices to retain in Eq. (18) the leading term of each sum. Then, for the range of diameters \( \approx 5 - 10 \text{ nm} \), \( l_0 \) can be expressed as follows:

\[
l_0 = (D_1 - D_2) \left[ \ln \left( \frac{HR_2}{HR_1} \frac{D_1 - 2\delta}{D_2 - 2\delta} \frac{N_{\text{FWHM}}^{(1)}}{N_{\text{FWHM}}^{(2)}} \right) \right]^{-1}.
\]

The effective identity of the \( d(\text{HR})/d(\text{volume fraction}) \) slopes characterizing the GNP’s of \( D_1 = 5 \text{ nm} \) and \( D_2 = 10 \text{ nm} \) implies \( HR_2/HR_1 \approx 1 \) in Eq. (18). For the contour \( \delta = 0.7 \text{ nm} \) deep, \( (D_1 - 2\delta)/(D_2 - 2\delta) \approx 0.42 \). The relation \( N_{\text{FWHM}}^{(1)}/N_{\text{FWHM}}^{(2)} \) follows from the straightforward counting of LAVMs that make a discrete spectrum on a circuar contour of the \( (D - 2\delta) \) size: how many of modes will fall within the FWHM of the longitudinal acoustic peak of gold. In principle, \( N_{\text{FWHM}} \) steadily increases with size, but the subtlety is that

---

2 The sum \( \sum_i N_{\text{FWHM}}^{(i)} \) takes into consideration contributions from the absorption of RF photons at phononic momenta \( \mathbf{q}, 2\mathbf{q}, i\mathbf{q} \) etc., in the spirit of Fig. 5 for fixed \( m_{\text{el}}/n_{\text{vm}} \) and \( \delta \).
not all steps in vibration energy are compatible with the energy conservation criteria Eq. (5, 6). Appendix B explains this situation and argues that $N_{FWHM}^{(1)} = 1$, $N_{FWHM}^{(2)} \approx 7.5$, hence $N_{FWHM}^{(1)}/N_{FWHM}^{(2)} \approx 0.13$, and from Eq. (19) $l_0 \approx -5$ nm/ln(0.055) = 1.72 nm.

Coming back to the discussion at this subsection’s opening, we can anticipate that the final HR, as function of GNP size, will be the interplay (multiplication) of three tendencies. The first one is the availability of “good” $D$ values which can contribute at all; they group around $\approx 7$ nm and rapidly become scarce at larger sizes. The second tendency is the number of LAVMs within the “good” energy interval (given by the elastic properties of gold); this number essentially grows with $D$. The third effect is an exponential cutting of the HR at the characteristic length much shorter than the electron mean free path in the bulk gold. In total, the last tendency shifts the maximum of HR($D$) a bit more to the left from the abovementioned “primary” $\approx 7$ nm value than the second tendency shifts it to the right.

One can infer that, would the data for $D < 5$ nm be available in Fig. 1 one could expect the initial slopes of the corresponding curves (of HR vs gold volume fraction) to go steeper. Correspondingly, the $l_0$ values for such sizes would likely be less than 1.72 nm, and, on the scale of the GNP sizes, the maximum of the HR would occur at slightly smaller values than so far reported.

We’ll see in the following how the final counting of HRs proceeds, which also takes into account a somehow delicate issue of possible “diversification” of the absorption / relaxation events.

D. Case of multiple contours

At a risk of attributing too much precision to a simple enough model, we would like to emphasize a possibility for the energy of excited electron to be returned to a “different” phonon than that it was originally borrowed from. Once a possibility for the energy of excited electron to be returned to a “different” phonon than that it was

Delicate issue of possible “diversification” of the absorption / relaxation events.

TABLE II Characteristics of internal contours and the electron path transversing them for several small values of $n_{vm}$. See text for details and refer to Fig. 11

| $n_{vm}$ | $n'_{vm}$ | $(D - 2\delta')/(D - 2\delta)$ | $l/(D - 2\delta)$ |
|----------|-----------|-------------------------------|-------------------|
| 2        | 1         | $1/2$                         | $1/4^a; 3/4^b$    |
| 3        | 1         | $1/3$                         | $1/3^d; 2/3^d$    |
| 3        | 2         | $2/3$                         | $1/6^f; 5/6^f$    |
| 4        | 1         | $1/4$                         | $3/8; 5/8$        |
| 4        | 2         | $2/4$                         | $2/8; 6/8$        |
| 4        | 3         | $3/4$                         | $1/8; 7/8$        |

Fig. 11 middle panel: $^a$AB, $^b$AC. Fig. 11 right panel: $^c$AC, $^d$AD, $^e$AB, $^f$AE.
in terms of the contour size. The values are listed in pairs, indicating that, as the electron traverses the GNP approximately along the diameter (by force of earlier invoked arguments), its “exit point” may occur on a close or on a remote point on a given internal contour.

Alternatively, a situation is imaginable that the resonance criteria of Eqs. (5, 6) allow a modification of electron energy step on exchange with a phonon, on respecting the condition

$$\frac{\nu h}{m_{el} \pi (D - 2\delta)} = \frac{\nu h}{m'_{el} \pi (D - 2\delta')}, \quad \text{hence} \quad \frac{D - 2\delta'}{D - 2\delta} = \frac{m'_{el}}{m_{el}}. \quad (21)$$

Since the last relation is < 1 (the secondary contour at depth $\delta'$ is deeper than the primary one), $m'_{el} > m_{el}$; moreover, $m'_{el}/m_{el}$ must be an integer.

Possible contributions to the HR, in the spirit of Eq. (17), are summarized in Table III and depicted in Fig. 12. The summation in the fourth column of Table III selects the cases ($m_{el}$ unchanged, $n'_{vm}$ variable) while that in the fifth column – the cases ($m'_{el}$ variable, $n_{vm}$ unchanged).

The condition $m'_{el} \leq 10$ combined with that of $m'_{el}/m_{el}$ to be integer does considerably restrict the amount of inner contours; hence so few non-zero entries in the fifth column of Table III. The largest contributions (for $D=6.65$ and 9.80 nm) come out because, with their small initial $m_{el}$ value, the largest number of contours (= 4) could be generated. The summation over possible contours and transitions yields a global

![FIG. 11 Schematically drawn cyclic contours within nanoparticles for three different values of the $n_{vm}$ parameter. “A” marks the excitation site for a Fermi electron on the outer contour, following the absorption of a RF photon and the LAVM. Other points indicate possible sites of relaxation of the excited electron on traversing the particle.](image)

![FIG. 12 Contributions of possible contours in GNP s of different sizes to their HR. Vertical lines mark the “individual” values of $N_{FWHM}^{(i)} \exp(-l_i/l_0)$ for each “valid” contour within a “resonant” GNP size, whereby thin black lines stand for contributions of the ($m'_{el}$ variable, $n_{vm} = \text{const}$) type, and thick orange lines – for contributions of the ($m_{el} = \text{const}, n'_{vm}$ variable) type. Light gray bars make a histogram of the abovementioned contributions, summed up within 2 nm steps of GNP diameter $D$.](image)
TABLE III Contributions to the HR from summations over primary and corresponding secondary contours characterized by different \((m_{el}, n_{vm})\) values in gold nanoparticles of diameters \(D\). See text for details.

| \(m_{el}\) | \(n_{vm}\) | \(D\) (nm) | \(\sum_i \equiv \sum_{n_{vm}, n_{vm}' \leq 10} N_{FWHM}^{(i)} \exp(-l_i/l_0)\) | \(\sum_i \equiv \sum_{m_{el}', m_{el} < m_{el}' \leq 10} N_{FWHM}^{(i)} \exp(-l_i/l_0)\) |
|---|---|---|---|---|
| 1 | 4 | 2.44 | 0.55 | 0 |
| 1 | 3 | 3.26 | 0.76 | 0 |
| 2 | 5 | 3.74 | 0.64 | 0 |
| 1 | 2 | 4.36 | 1.10 | 0 |
| 4 | 7 | 4.75 | 0.45 | 0 |
| 3 | 5 | 4.90 | 0.50 | 0 |
| 2 | 3 | 5.22 | 0.82 | 0 |
| 5 | 7 | 5.45 | 0.72 | 0 |
| 3 | 4 | 5.61 | 1.41 | 0 |
| 5 | 6 | 5.98 | 0.92 | 0 |
| 1 | 1 | 6.65 | 0.24 | 4.62 |
| 8 | 7 | 7.18 | 0.42 | 0 |
| 7 | 6 | 7.26 | 1.34 | 0 |
| 5 | 4 | 7.55 | 0.87 | 0 |
| 9 | 7 | 7.67 | 0.18 | 0 |
| 4 | 3 | 7.83 | 0.79 | 0.45 |
| 10 | 7 | 8.14 | 0.31 | 0 |
| 3 | 2 | 8.36 | 1.51 | 1.10 |
| 5 | 3 | 8.86 | 0.61 | 0.38 |
| 7 | 4 | 9.11 | 1.24 | 0 |
| 2 | 1 | 9.80 | 0.06 | 3.13 |
| 9 | 4 | 10.44 | 0.94 | 0 |
| 7 | 3 | 10.65 | 0.50 | 0 |
| 5 | 2 | 11.06 | 1.10 | 0.52 |
| 8 | 3 | 11.45 | 0.42 | 0 |
| 3 | 1 | 12.19 | 0.02 | 1.48 |
| 10 | 3 | 12.90 | 0.36 | 0 |
| 7 | 2 | 13.24 | 0.93 | 0 |
| 4 | 1 | 14.21 | 0.01 | 1.00 |
| 5 | 1 | 15.98 | 0 | 0.79 |
| 6 | 1 | 17.58 | 0 | 0 |
| 7 | 1 | 19.06 | 0 | 0 |
| 8 | 1 | 20.43 | 0 | 0 |
| 9 | 1 | 21.71 | 0 | 0 |
| 10 | 1 | 22.93 | 0 | 0 |

scan of the property \(\sum_i N_{FWHM}^{(i)} \exp(-l_i/l_0)\) which is expected to be proportional to the HR, as function of the GNP diameter. The results are shown in Fig. 12 in two ways: as a contribution (weighted by \(\exp(-l_i/l_0)\)) of each relaxation event, possible in a GNP of given size, and as cumulate effect of multiple events, grouped in a histogram with a fixed step in \(D\). The first representation indicates that the contributions start from \(D = 2.44\) nm and drop down to zero beyond \(D = 15.98\) nm. The histogram representation seems more helpful in inspecting the “importance” of different GNP sizes for the HR. It seems that the HR efficiency
peaks around $D \approx 6$ nm and rapidly decreases for smaller and larger diameters.

To conclude the discussion about multiple contours, we point out that the excitation energy for an electron can also be borrowed from LAVM propagating along one of internal contours. However, the probability of such effects rapidly decreases with descending onto ever shorter contours characterized by ever sparser distribution of quantized resonance modes.

IV. ON THE REDUCED HEAT PRODUCTION IN AGGREGATED GNPS

An aggregation of $n$ GNPs yields a larger particle, with the number of atoms and electrons increased by the factor of $n$. However, this won’t be normally accompanied by a formation of joint subsurface contour at the depth $\delta$, as the core regions of different GNPs remain isolated from each other by their surface shells. Therefore the “optimal” conditions of RF photon absorption, given by Eqs. (5) and (6), would be violated, and the HR of aggregated GNPs reduced.

After Fig. 1, the HR eventually saturates, for all particle sizes, as function of gold volume fraction. For small GNPs this saturation occurs faster, for the apparent reason that, for a given gold volume fraction, smaller particles mean their higher concentration, and hence higher tendency for aggregation.

V. FURTHER SUGGESTIONS FOR ENHANCING HEATING RATES IN GNPS

In Sec. III, it has been shown that in GNPs, the HR is enhanced thanks to large number of participating LAVMs. As heating of GNPs involves both the LAVMs and the Fermi electrons, one way of enhancing the HR ever further would be to increase the number of electrons absorbing the RF photons. This is possible through enhancing the local electronic DOS (EDOS) at the Fermi energy of gold, doping the latter with transition metal impurities, e.g., Ta or Fe—see Fig. 13 and also (Moldosanov and Postnikov 2013; Postnikov and Moldosanov 2012). The main peaks of spin-split local EDOS of these impurities, according to first-principles calculations, are pinned at the Fermi level of gold, adding substantially to the bulk EDOS of the latter. In addition to just increasing the number of electrons absorbing the RF photons, such doping would also enhance the scattering intensity of excited electrons. Both of these tendencies are expected to result in enhanced HR.

![FIG. 13 Calculated spin-resolved local EDOSs against energy relative to $E_F$ for Ta and Fe impurities in Au, reproduced from (Postnikov and Moldosanov 2012). Calculated EDOS of (Muñoz et al. 2013) for Fe $d$-electrons in 32-atom quasirandom structure of Au$_{30}$Fe$_2$ supports our results for Fe impurities in Au (Postnikov and Moldosanov 2012).](image)

3Our calculations were done within the density functional theory, using the generalised gradient approximation for the exchange-correlation, by the SIESTA method (see [http://departments.icmab.es/leem/siesta/]), allowing full atom relaxation for the 64-atom supercell ($4\times4\times4$-replicated fcc primitive cell with one atom substituted by impurity).

4The calculations done on 64-atom super cells (one impurity of Ta or Fe per 63 Au atoms) indicate that the total EDOS at the Fermi level is increased by $\sim 50\%$ compared to the pure Au.
Another imaginable way to bring about high EDOS would be due to $f$-electronic states residing at the Fermi level, that is the case of heavy-fermion compounds – see [Stewart 1984] for a review. Such compounds, typically possessing a rare-earth element as their essential constituent, exhibit an anomalously high residual resistivity at low temperatures, traceable to high electron scattering intensity, and, in its turn, to a strong peak in the density of states of $f$ electrons at the Fermi level. The presence of the compound CeCu$_6$ among heavy-fermion systems permits to presume that gold, like a homologue of copper, may host $f$-element atoms so as to give rise to heavy-fermion behaviour. The nanoparticles of such compounds might possess a yet elevated heating rate.

VI. DISCUSSION

The analysis of conservation conditions for energy ($m_{el} \Delta E_{el} \approx n_{vm} \Delta E_{vm}$, and momentum (i.e., for the movement direction of the excited electron after absorption of the RF photon and the LAVM) lets estimate the size of GNPs capable to produce high HR via a simultaneous involvement of several vibration modes with energies matching $n_{vm} \Delta E_{vm}$, situated within the LAVMs of gold. It follows from our estimates that the optimal size of GNPs to use in RF hyperthermia is $5 \sim 7$ nm.

A number of known results seem to support our argumentation. [Moran et al. 2009], who explored heating of GNP's with sizes from 5 to 250 nm in the electric field of 13.56 MHz frequency, observed that the highest HR was inherent to GNP's of 5 nm size. [Kruse et al. 2011] heated the GNP's by the 13.56 MHz electric field too, and, again, the smallest tested GNP's ($\approx 5$ nm size) revealed the maximum HR.

Other researches testify that as the GNP's sizes deviate from $5 \sim 7$ nm, the HR's change from bad to worse. [Yurdock and Hussain 2010] observed the heating of GNP's with the 4 nm and 13 nm diameters and pointed out that their HR's were several times lower than those for the 5 nm GNP's in the work by [Moran et al. 2009]. [Li et al. 2011] exposed the GNP's with sizes of 20, 50 and 200 nm to the 13.56 MHz electric field and did not observe heating. In view of our analysis, the GNP's of 20 or 50 nm fall short of sizes (shown in Table 1) that would enable a “direct” absorption of a RF photon; at the same time, these sizes are much larger than $5 \sim 7$ nm, the “optimum” diameter for the phonon-assisted absorption. As for the 200 nm size, that falls close to a number appearing in Table 1, one can presume that the resonance for direct absorption is quite sharp and not satisfied in the real GNP's studied.

[Liu et al. 2012] did not detect any significant heating of GNP's with sizes of 15 to 30 nm (i.e. larger than the optimum size) at the 13.56 MHz frequency. [Sirotkina et al. 2012] tried to treat tumours by the RF radiation of frequency 2.45 GHz using the gold nanorods of 30 nm diameter and 60 nm length, whereby no anticancer effect was identified. In our opinion, namely the large sizes of nanorods were the problem. [Corr et al. 2012a] and [Raoof et al. 2012] pointed out that heat generation was significantly reduced when the GNP's were aggregated. We attribute it to the fact that, as the GNP's come in contact, the common size of the formed aggregate is increased, and the condition (5) is not anymore fulfilled, resulting in reduction of HR's of GNP's.

A valuable contribution to the analysis of experimental and theoretical studies in heating kinetics of GNP's in the RF range was offered by a recent work by [Letfullin et al. 2015]. The authors have noted a spectacular failure of previous theoretical conclusions to account for the experimental evidence that RF radiation is capable of heating the GNP's. Our present work that emphasises the crucial role of LAVM's in the RF absorption suggests a plausible explanation of the above problem.

[Leifert et al. 2013] who studied in vivo the size dependence (within the 2 to 15 nm range) of the GNP's localization and penetration in cancer cells, multicellular spheroids and tumours, concluded that the 2 and 6 nm GNP's demonstrated advantages over larger nanoparticles in terms of tumour uptake and permeability. Such GNP's were able to penetrate deeply into tumour tissue and provide high levels of accumulation in it. As an application of the smallest ($\sim 2$ nm size) GNP's seems questionable due to loosening their biocompatibility [Leifert et al. 2013; Pan et al. 2012; Pan et al. 2007], the 5 $\sim 7$ nm GNP's, possessing also the highest HR's, become very valuable instruments in the RF hyperthermia.

Throughout the whole range of frequencies $\nu$ used in medical or biological studies ($\nu \sim 10$ MHz $\sim 3$ GHz), the RF photon energies $h \nu$ are small compared to $n_{vm} \Delta E_{vm}$ of Eq. (5), for the LAVM's energy range of $\approx 3$ $\sim 21$ meV. Consequently, the condition (5) is generally satisfied, and the GNP's of about $5 \sim 7$ nm size would have elevated HR's not only at 13.56 MHz, but everywhere within the mentioned interval of frequencies; in particular, at 2.45 GHz, the operation frequency of a domestic microwave oven with fine, inverter-regulated
power control. The use of the latter for laboratory investigations would permit performing genetic and biological experiments in vivo—e.g., with GNPs immersed in the tissues of larvae of such classical research target as Drosophila melanogaster.

Recently, San et al. (2013) reported that at the frequency of 0.35 MHz the Pt nanoparticles possessed HR twice higher than that of the GNPs and proposed to use them in RF hyperthermia. We attribute high HR of Pt nanoparticles to enhanced EDOS at the Fermi level of Pt, as compared to Au. For this reason, in Pt, a number of electrons able to absorb the RF photons is enhanced.

One should expect that in conditions of the experimental capacitive electric transfer system used by San et al. (2013) in nanoparticles of AuPd and AuPt alloys (Pd and Pt content within 40 – 70 mass %), the HRs would be even higher than those in Pt nanoparticles. This is because in these alloys, judging by their enhanced EDOS at $E_F$, the intensity of scattering of Fermi electrons is higher than that in pure Pt. However, an application of AuPd, AuPt, Pd and Pt nanoparticles in the RF hyperthermia is questionable due to their enhanced catalytic activities.

Compared with these nanoparticles, the GNPs containing impurities of Ta and/or Fe, and hence developing an enhanced EDOS at the Fermi level and, expectedly, an enhanced intensity of electron scattering, seem to be much more promising for the RF hyperthermia using the GNPs (Moldosanov and Postnikov, 2013; Postnikov and Moldosanov, 2012).

During last years, the use of GNPs as systems of drug and gene delivery into cancer cells has expanded considerably. An opportunity to synergistically combine these techniques with RF hyperthermia may open new terrains in contemporary cancer theranostics. Recently Conde et al. (2015), apparently driven by a need to sense and overcome the cancer multidrug resistance, invented an implantable hydrogel with embedded DNA-coated GNPs of $\sim$10 – 17 nm diameters. Our above discussion hints that an attempt to go towards slightly smaller particles, of 5 – 7 nm diameter, would “activate” the embedded GNPs for the RF hyperthermia, adding such an option to the GNPs’ other functions.

Another issue that enters the domain of feasible is the transfer of technologies developed for the plasmonic heating of GNPs onto the RF range. Zharov and co-workers (Galanzha et al. 2009; Nedosekin et al. 2013) reported that at the frequency of 0.35 MHz the Pt nanoparticles possessed HR twice higher than that of the GNPs and proposed to use them in RF hyperthermia. We attribute high HR of Pt nanoparticles to enhanced EDOS at $E_F$, the intensity of scattering of Fermi electrons is higher than that in pure Pt. However, an application of AuPd, AuPt, Pd and Pt nanoparticles in the RF hyperthermia is questionable due to their enhanced catalytic activities.

Another recent work by (Tsai et al. 2015) outlines the use of gold nanorods (of 10 nm diameter / 41 nm length) connected to nanodiamonds, whereby the gold part serves to hyperthermia, by near-infrared laser heating, and the nitrogen-vacancy centers in diamond serve for temperature sensing. Here again, the use of nanoparticles of 5 – 7 nm size in place of nanorods would hopefully help to extend this technique over RF-induced hyperthermia.

Last but not least, the RF heating of GNPs may be of interest for developers of therapeutic strategies targeting to inhibit amyloidogenic process in the Alzheimer’s disease. Araya et al. (2008) suggested to use in this context the GNPs of 12.5±1.7 nm size heated by the microwave 14 GHz radiation. Chances are that
using the GNPs of “optimal” sizes would be useful for these tasks, too.

VII. CONCLUSION

We suggest a physical model of the size effect in heat generation in GNPs, which also accounts for a reduction of heat generation as the GNPs get aggregated. In this model, the LAVMs (dominating in the distribution of vibrational density of states) play an important role – an apparently novel element in the related theory framework. According to our model, the heating of GNPs is thought to consist of two consecutive processes: first, the Fermi electron absorbs simultaneously the RF photon and the LAVM available in the GNP; hereafter the excited electron is relaxed, exciting a LAVM with the energy higher than that of the previously absorbed LAVM. The model predicts that the GNPs to be effectively heated should possess diameters of \( \sim 5 \text{–} 7 \text{ nm} \), i.e., very close to the experimentally inspected \( \sim 5 \text{ nm} \). The absorption band is expected to be very wide (\( \sim 10 \text{ MHz} \text{–} 3 \text{ GHz} \)). This allows the use of frequencies typical for the “conventional” RF hyperthermia (without conducting nanoparticles). The energy release in the GNPs can be optimized by tuning the RF frequency, searching a compromise between the HR energy transfer efficiency and a penetration depth of the RF radiation into the biological tissue. The GNPs containing Ta or Fe impurity atoms are expected to be more effective heaters compared to nanoparticles of pure gold, due to enhanced electron density of states at the Fermi level. Gold nanoparticles with rare-earth impurity atoms are also brought into consideration as promising for the RF hyperthermia with conducting nanoparticles. The significance of the present study follows from the fact that the cancer specialists seeking approval for human clinical trials on the basis of their experimental results remain thus far in the dark in what regards the physical mechanism behind the observed trends.

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Appendix A: Level spacing vs number of atoms in a GNP

(Kubo [1962, 1977]) adopted the one-electron approximation to electrons in small metallic particles, whereupon D.Y. [Sun et al. 2001] predicted and J. [Sun et al. 2014] experimentally demonstrated the existence of the bulklike core region in them. This justifies considering the GNP as a crystalline one and permits to specify a relationship between the level spacing of electrons and number of atoms in GNP, using formulas for the free electron gas. A GNP of cuboid shape and consisting of \( N_a \) atoms contains (one “free” electron per atom of gold) \( N_e \) electrons filling the energy levels up to the Fermi energy \( E_F \). The free-electron EDOS is (e.g., Wert and Thomson [1970]):

\[
\rho(E) = \frac{dN'}{dE} = 4\pi(2m)^{3/2} L^3 E^{1/2} h^{-3},
\]

(A1)

where \( dN' \) is a number of states within the energy interval \( dE \), \( L \) is the cuboid’s edge and \( h \) the Planck constant. Then the total number of electrons is

\[
N_a = \int_0^{E_F} \rho(E) \, dE = \frac{8\pi}{3} (2m E_F)^{3/2} \left( \frac{L}{h} \right)^3.
\]

(A2)

In accordance with Eq. (A1), the spacing \( \Delta E_{el} \) between the Fermi level and nearest energy level above it equals \( \Delta E_{el} \approx \Delta N' / \rho(E_F) \), where \( \Delta N' = 2 \), hence

\[
\Delta E_{el} \approx \frac{2}{\rho(E_F)} = \frac{h^3}{2\pi(2m)^{3/2}L^3 E_F^{1/2}}.
\]

(A3)
From Eqs. (A2) and (A3), the Kubo’s formula is deduced:

\[ \Delta E_{el} \approx \frac{4}{3} \frac{E_{F}}{N_{a}}. \]  \hspace{1cm} (A4)

Appendix B: Counting vibration modes in GNPs of given size, within given energy range

Assuming that the LAVMs propagate with (longitudinal) sound velocity \( v_L \) along the circular contour at depth \( \delta \) under the surface of spherical particle of diameter \( D \), the phonon energy quantum is \( \Delta E_{vm} = v_{L} b / [\pi (D - 2\delta) ] \). However, insofar as phonons are absorbed /created in the process of the electron excitations / relaxations, the phonon energies can only change in blocks, commensurable with the electron states quantization, i.e., respecting the energy conservation condition of Eq. (5). \( n_{el} \Delta E_{el} \approx n_{vm} \Delta E_{vm} \). Only certain combinations \((n_{el}, n_{vm})\) are possible, that selects the “resonant” values of \( D \), as given by Eq. (11). Table III lists the allowed groups \((n_{el}, n_{vm}, D)\) in the increasing order of \( D \).

Searching in Table III for the \( D \) values closest to the “reference” ones \( D_1 = 5 \text{ nm} \) and \( D_2 = 10 \text{ nm} \), one finds \( D = 5.22 \text{ nm} \) that comes along with \( n_{vm} = 3 \), and \( D = 9.80 \text{ nm} \) that comes along with \( n_{vm} = 1 \). We note that the apparently “competitive” values of \( D \) by their closeness to the reference values, namely, \( D = 4.90 \text{ nm} \) and \( 10.44 \text{ nm} \), can only be selected with much higher values of \( n_{vm} \) and, consequently, may only intervene with much sparser distribution, and hence much smaller impact, or their allowed vibration modes. For \( D = 5.22 \text{ nm} \), \( n_{vm} \Delta E_{vm} = 3.35 \text{ meV} \), so there is no more than just one vibration mode, of the energy \( 5 \times (n_{vm} \Delta E_{vm}) \), that falls within the FWHM range of the interest, 14.6 to 18.4 meV (see caption to Fig. 5 and the related text), hence \( N_{FWHM}^{(1)} = 1 \) in Eq. (19). For \( D = 9.80 \text{ nm} \), \( (n_{vm} = 1) \Delta E_{vm} = 0.51 \text{ meV} \), and the above cited FWHM range may hosts much more modes at multipliers of this energy, namely, \( N_{FWHM}^{(2)} \approx 7.5 \) in Eq. (19).

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