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Noninertial mechanism for electronic energy relaxation in nanocrystals

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The low-frequency vibrational spectrum of an isolated nanometer-scale solid differs dramatically from that of a bulk crystal, causing the decay of a localized electronic state by phonon emission to be inhibited. We show, however, that an electron can also interact with the rigid *translational* motion of a nanocrystal. The form of the coupling is dictated by the equivalence principle and is independent of the ordinary electron-phonon interaction. We calculate the rate of nonradiative energy relaxation provided by this mechanism and establish its experimental observability.

The dominant mechanism for the low-energy decay of a localized electronic impurity state in a macroscopic semiconductor or insulator is usually phonon emission.[1,2] In an isolated nanometer-scale crystal, however, the reduced dimensionality causes a suppression of the vibrational density-of-states (DOS) at low energies.[3] In particular, in a spherical nanoparticle of diameter d there will be an acoustic phonon energy gap $\Delta\omega$ of the order of $2\pi v/d$, where v is a characteristic sound velocity of the bulk crystal. The one-phonon energy relaxation rate of an electron in the excited state of a two-level system with energy spacing $\Delta\epsilon$ therefore vanishes (or is greatly suppressed) when $\Delta\epsilon$ is less than $\Delta\omega$.[4] Indeed, a dramatic suppression of the phonon-induced exciton dephasing rate[5,6] and nonradiative relaxation rate[7–9] has been observed in nanocrystalline systems.

Nanoparticles are usually coupled to an environment consisting of other nanoparticles, a glass or polymer support matrix, or a solid substrate, and this mechanical interaction can modify a nanoparticle's low-frequency vibrational spectrum.[10] Figure 1 shows a transmission-electron-microscope image of a cluster of 15 nm Y_2O_3 nanoparticles prepared by gas-phase condensation. Although little is known in detail about the effects of environmental interaction on electronic energy relaxation in nanoparticles,[11] it is clear that for the case of a nanoparticle only *weakly* coupled to other nanoparticles or to a substrate, phonon emission will still be prohibited because the low-frequency modes introduced by interaction with the environment will involve mostly *rigid* center-of-mass (c.m.) motion of the nanoparticles, which produces no strain. For example, Fig. 2 shows the collective-mode DOS for a model (illustrated in the inset) of the nanoparticle cluster of Fig. 1. Although the cluster possesses modes at frequencies less than $\Delta\omega$, which is about 10 cm^{-1} for these nanoparticles, these modes cannot couple to an impurity state through ordinary electron-phonon interaction.

In this paper we propose a nonradiative relaxation mechanism caused by the *inertial* coupling of an electron to the nanoparticle's translational c.m. motion. This interaction is present because an electron bound to an impurity center in an oscillating nanoparticle is in an accelerating reference frame, and, in accordance with Einstein's equivalence principle, it feels a fictitious time-dependent force. We shall show below that this relaxation mechanism is operative even at zero temperature, owing to the fact that quantum zero-point motion of the c.m. is sufficient to produce the fictitious force.

In what follows we shall analyze the simplest nanoparticle model displaying this effect; more sophisticated models, as well as the influence of inertial coupling on other dynamical processes such as dephasing, are subjects of on-going investigations and will be discussed in future publications. The present model consists of a single nanoparticle of mass M connected to a bulk substrate by a few atomic bonds. The effect of the substrate is to subject the nanoparticle to a one-dimensional harmonic oscillator potential $V=\frac{1}{2}M\Omega^2X^2$ with frequency Ω, the X direction being perpendicular to the plane of the substrate. However, because the c.m. motion is that of a macroscopic harmonic oscillator interacting with many other degrees of freedom, such as the phonons of the bulk substrate, it is necessary on physical grounds to include energy dissipation (friction) of that oscillator. Possible rotational motion of the nanoparticle is not important here and will be ignored.[12]

Denoting the c.m. of the nanoparticle by $\mathbf{R}$, a Hamiltonian in the c.m. frame can be obtained by rewriting the time-dependent Schrödinger equation in terms of new coordinates $\mathbf{r}'=\mathbf{r}-\mathbf{R}$ and $t'=t$. After a series of gauge transformations we obtain

$$\begin{aligned} H_{\mathrm{c.m.}} = {} & \sum_{\alpha} \epsilon_\alpha c_\alpha^\dagger c_\alpha + \sum_n \omega_n a_n^\dagger a_n + \Omega b^\dagger b \\ & + \sum_{n\alpha\alpha'} g_{n\alpha\alpha'} c_\alpha^\dagger c_{\alpha'} (a_n + a_n^\dagger) \\ & - g \sum_{\alpha\alpha'} x_{\alpha\alpha'} c_\alpha^\dagger c_{\alpha'} (b + b^\dagger) + \Delta H. \end{aligned} \tag{1}$$

The first term in Eq. (1) is the Hamiltonian for a noninteracting two-level system; the other electronic levels can be neglected with no loss of generality. Here ϵ_α (with $\alpha=1,2$) are the energy levels of the localized impurity state, $c_\alpha^\dagger$ and c_α are electron creation and annihilation operators.[13] The second term in Eq. (1) describes the nanoparticle's *internal* vibrational dynamics. The ω_n are the frequencies of the internal modes, and the $a_n^\dagger$ and a_n are the corresponding phonon creation and annihilation operators. For the case of a perfectly spherical nanoparticle the vibrational eigenmodes

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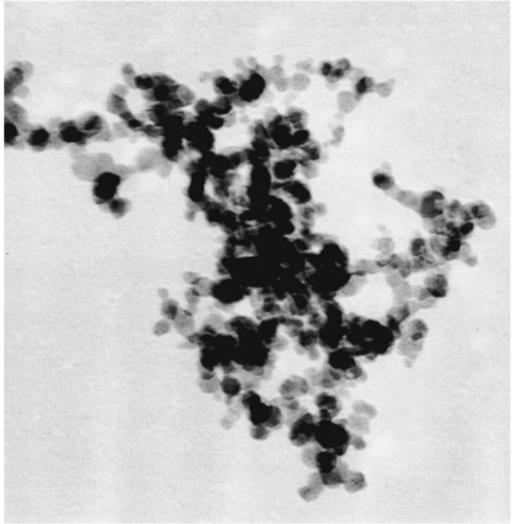

FIG. 1. Cluster of Y_2O_3 nanoparticles. The mean particle diameter is approximately 15 nm.

and eigenvalues can be obtained analytically within continuum elasticity theory;[14,15] the frequency of the lowest internal mode (a fivefold degenerate torsional mode) is approximately $2\pi v_t/d$, where v_t is the bulk transverse sound velocity and d is the diameter. These internal vibrational modes have been observed by low-frequency Raman scattering[16–20] and by femtosecond pump-probe spectroscopy.[21]

The third term in Eq. (1) describes the harmonic dynamics of the c.m. As discussed above, the nanoparticle is assumed to be constrained to move in the x direction only. Hence, the c.m. translational motion is described by a single bosonic degree-of-freedom

$$b \equiv \sqrt{\frac{M\Omega}{2}}\left(X + \frac{i}{M\Omega}P\right), \tag{2}$$

where X and P are the x components of the c.m. position and momentum.

The fourth term in $H_{\mathrm{c.m.}}$ is the ordinary leading-order interaction between the two-level system and the internal vibrational modes. Here $g_{n\alpha\alpha'}$ is the electron-phonon coupling constant; it depends on the detailed microscopic structure of the nanoparticle, the nature and position of the impurity, and the spatial dependence of the internal vibrational modes. In the regime of interest here, where phonon emission is inhibited, this electron-phonon interaction term can be ignored, and the remaining Hamiltonian is that of a two-level atom in a cavity with a single damped mode.[22]

The fifth term in Eq. (1), which describes the inertial coupling between the two-level system and the c.m. motion, is the focus of the present work. Here $x_{\alpha\alpha'} \equiv \langle \phi_\alpha | x | \phi_{\alpha'} \rangle$ are dipole-moment matrix elements, which, of course, depend on the form of the impurity states $\phi_\alpha(\mathbf{r})$, and

$$g \equiv \sqrt{\frac{m^2\Omega^3}{2M}} \tag{3}$$

is a coupling constant that depends only on the (bare) electron mass m and on macroscopic properties of the nanoparticle. The presence of this fifth term can be understood as follows: The Hamiltonian for the noninteracting two-level system, the first term in $H_{\mathrm{c.m.}}$, is written in a coordinate system moving with the oscillating nanoparticle, which is a *noninertial* reference frame. According to the equivalence principle,[23] the electron therefore sees an additional uniform force

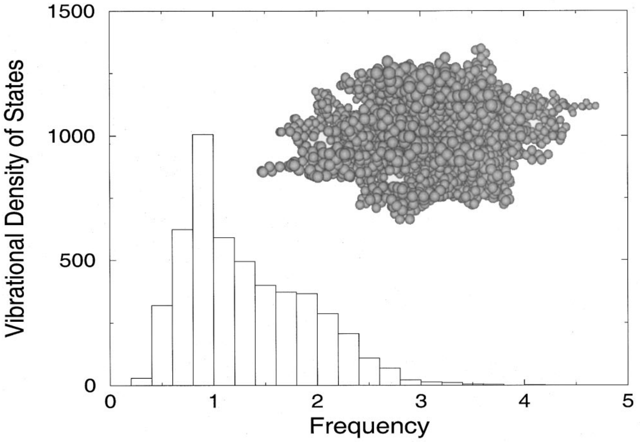

FIG. 2. Histogram of the number of vibrational modes per unit frequency of a model nanoparticle cluster, shown in the inset. The frequency is given in wavenumbers. The cluster contains about 1300 nanoparticles of identical mass M, and between each adjoining nanoparticle is a harmonic spring with a stiffness k chosen such that $\sqrt{k/M}$ is equal to 1 cm^{-1}.

$$\mathbf{F}_{\mathrm{eff}} = -m\ddot{\mathbf{R}}, \tag{4}$$

where, as before, $\mathbf{R}$ is the nanoparticle c.m. For the case of harmonic motion, Eq. (4) can be written as $\mathbf{F}_{\mathrm{eff}} = m\Omega^2\mathbf{R}$. Thus, the potential energy of an electron at position $\mathbf{r}$ in the c.m. frame is

$$U = -m\Omega^2\mathbf{R}\cdot\mathbf{r}, \tag{5}$$

which, in one dimension, is equivalent to the fifth term in Eq. (1). Although spin indices have been suppressed in Eq. (1), it should be understood that the inertial coupling between the electron and the c.m. motion conserves spin.

The final term in Eq. (1), denoted by ΔH, describes an interaction between the nanoparticle's translational motion and a bath of other harmonic oscillators, such as the phonons of the bulk substrate or the c.m. degrees-of-freedom of other nanoparticles.[24] The effect of ΔH is to dissipate energy from the oscillating nanoparticle. In the absence of this damping, the inertial coupling causes energy to be continuously exchanged between the two-level system and the c.m. oscillator in a Rabi-like fashion; this interesting dissipation-free limit, although not relevant for the nanoparticle systems considered here, will be discussed in detail elsewhere.

To study the effect of the fifth term in Eq. (1) on the electronic energy relaxation rate we calculate the electron self-energy perturbatively.[25] We assume that $\Delta\epsilon$ is sufficiently smaller than $\Delta\omega$ so that ordinary phonon emission is prohibited; this allows us to set $g_{n\alpha\alpha'} = 0$. The leading-order self-energy is

$$\Sigma(\alpha,i\omega)=-\frac{g^2}{\beta}\sum_{\omega_B}\sum_{\alpha'}|x_{\alpha\alpha'}|^2G_0(\alpha',i\omega-i\omega_B)D(i\omega_B), \tag{6}$$

where β is the inverse temperature, ω_B is a bosonic Matsubara frequency, $G_0(\alpha,i\omega)=(i\omega-\epsilon_\alpha)^{-1}$ is the noninteracting electron Green's function, and $D(i\omega_B)$ is the Fourier transform of a phonon propagator

$$D(\tau)\equiv-\langle T[b(\tau)+\overline{b}(\tau)][b(0)+\overline{b}(0)]\rangle \tag{7}$$

that has been renormalized to include the effects of ΔH. The precise form of $D(i\omega_B)$ depends, of course, on ΔH, and in the absence of a reliable microscopic model for ΔH we shall use a (retarded) propagator of the form

$$D^R(\omega)=\frac{1}{\omega-\Omega+i\gamma}-\frac{1}{\omega+\Omega+i\gamma}, \tag{8}$$

which has a Lorentzian spectral function of width γ.

The relaxation rate $\tau^{-1}\equiv-2\,\mathrm{Im}\,\Sigma^R(\alpha,\epsilon_\alpha)|_{\alpha=2}$ of the excited state at zero temperature is found to be

$$\tau^{-1}=2\pi g^2|x_{12}|^2f(\Delta\epsilon-\Omega), \tag{9}$$

where $f(\omega)\equiv\gamma/\pi(\omega^2+\gamma^2)$ is a Lorentzian function of width γ. The fact that relaxation occurs even at zero temperature, when the nanoparticle c.m. is in its ground state, shows that zero-point c.m. motion is sufficient to produce a fictitious force.

When the energy separation $\Delta\epsilon$ between the two levels is resonant with the frequency Ω of the translational mode, the electronic relaxation rate becomes

$$\tau_{\mathrm{res}}^{-1}=4g^2|x_{12}|^2\tau_{\mathrm{c.m.}}, \tag{10}$$

where $\tau_{\mathrm{c.m.}}\equiv1/2\gamma$ is the lifetime of the translational mode. This can be written (reinstating factors of $\hbar$) as

$$\tau_{\mathrm{res}}^{-1}\approx1.6\times10^{-21}\frac{Q\Omega_0^2X^2}{M}\ \mathrm{s}^{-1}, \tag{11}$$

where $Q\equiv\tau_{\mathrm{c.m.}}\Omega$ is the quality factor of the c.m. oscillator, Ω_0 is the c.m. oscillation frequency in measured in wavenumbers, X is the dipole moment measured in Bohr radii, and M is the nanoparticle mass measured in grams.

We believe that it should be possible to observe this relaxation mechanism by means of an infrared quantum counter experiment[26] in $\mathrm{LaF_3{:}Ho^{3+}}$ nanoparticles. The Ho^{3+} $^5I_8(\mathrm{II})$ level is 4.5 cm^{-1} above the ground state and can be excited using a pulsed far infrared source. The population of the $^5I_8(\mathrm{II})$ state can be probed by a pulsed visible laser tuned to the $^5I_8(\mathrm{II})\rightarrow{}^5S_2(\mathrm{I})$ transition; a measurement of the intensity of the $^5S_2(\mathrm{I})$ emission as a function of the delay between the far infrared and optical pulses would enable the relaxation of the $^5I_8(\mathrm{II})$ to be observed. The resonant relaxation rate for a $\mathrm{LaF_3}$ nanoparticle with 10 nm diameter is approximately

$$\tau_{\mathrm{res}}^{-1}\approx1.0\times10^{-2}\ \mathrm{s}^{-1}\quad\text{for}\quad Q=10^2 \tag{12}$$

and

$$\tau_{\mathrm{res}}^{-1}\approx1.0\times10^{2}\ \mathrm{s}^{-1}\quad\text{for}\quad Q=10^6. \tag{13}$$

The second estimate applies to a very weakly damped nanoparticle. It is simple to show that, for this nanoparticle, the maximum Q factor allowed by the perturbative analysis leading to Eq. (9) is about 10^8 (see Ref. 25). Although small, these rates are still much larger than the radiative rate between these closely spaced levels.

In conclusion, our analysis shows that fictitious forces produce a coupling between an impurity state in a doped nanoparticle and the rigid-body c.m. motion. If the c.m. oscillation frequency is near (on the scale of γ) to the level separation $\Delta\epsilon$, this effect provides a mechanism for energy relaxation even when conventional phonon emission is prohibited. We find that on resonance the relaxation rate is proportional to the translational mode lifetime $\tau_{\mathrm{c.m.}}$: This means that relaxation is faster when the translational mode is weakly coupled to its environment, whereas coupling to an appreciably damped c.m. mode is less effective. Although we do not believe that the mechanism proposed here is responsible for the energy relaxation observed in Refs. 8 and 9, our estimates clearly show that this somewhat exotic phenomenon is experimentally accessible.

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