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Sylvain DUCOTTET, Adil EL BAROUDI - Small-scale effects on the radial vibration of an elastic nanosphere based on nonlocal strain gradient theory - Nanotechnology - Vol. 34, n°11, - 2023

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Small-scale effects on the radial vibration of an elastic nanosphere based on nonlocal strain gradient theory

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Abstract

Nonlocal strain gradient theory is widely used when dealing with micro- and nano-structures. In such framework, small-scale effects cannot be ignored. In this paper a model of radial vibration of an isotropic elastic nanosphere is theoretically investigated. The frequency equation is obtained from a nonlocal elastic constitutive law, based on a mix between local and nonlocal strain. This model is composed of both the classical gradient model and the Eringen's nonlocal elasticity model. To check the validity and accuracy of this theoretical approach, a comparison is made with the literature in certain specific cases, which shows a good agreement. Numerical examples are finally conducted to show the impact of small-scale effects in the radial vibration, which need to be included in the nonlocal strain gradient theory of nanospheres. It reveals that the vibration behavior greatly depends on the nanosphere size and nonlocal and strain gradient parameters. Particularly, when the nanospheres radius is smaller than a critical radius, the small-scale effects play a key role. Thus, the obtained frequency equation for radial vibration is very useful to interpret the experimental measurements of vibrational characteristics of nanospheres.

Keywords: nonlocal strain gradient theory, radial vibration, analytical method

List of relevant symbols

σ	Total stress tensor
α_0, α_1	Nonlocal kernel functions
ξ_0, ξ_1	Nonlocal parameters
e_0, e_1	Nonlocal material constants
b	Internal characteristic length
ζ	Strain gradient parameter
ε	Strain tensor
C	Fourth order elasticity tensor
\mathbf{u}	Displacement field
u	Radial displacement
ρ	Density
λ, μ	Lame parameters
c_l	Longitudinal wave velocity
c_t	Transverse wave velocity
ϕ	Potential displacement
\mathbf{e}_r	Unit vector
ω	Angular frequency
a	Nanophere radius
σ_{rr}	Radial stress component

1. Introduction

During the last decades, vibrational properties of nano-particles have been widely studied with both fundamental [1–3] and technological [4, 5] motivations. These vibrations have been observed by a variety of experimental techniques

[6–9]. These experimental techniques, namely, time-resolved and Raman spectroscopies aim at studying the vibrations of nanoparticles in a large range of size, shape, and environment conditions. The vibrational signature of nano-structures offers many possibilities for their *in situ* characterization (for instance to determine their size [10], size dispersion [11], or shape anisotropy [12]) and is a unique means for investigating their interaction with their environment [13, 14].

Particularly, studying vibrations in noble-metal spherical nanoparticles has several interests [15, 16]. First, the choice of a spherical geometry is not innocuous. Because of numerous analytical solutions available for such a geometry, nanospheres have been thoroughly investigated [17–19]. Lamb used this geometry and found a proportionality between the period of the symmetric radial mode and the radius of the spherical particle [20]. This proportionality has been verified for gold nanoparticles [2, 21].

Besides, the choice of noble-metal materials is justified by the interesting properties it provides. With this kind of nanoparticles, we note a strong modulation of optical absorption and scattering thanks to links between vibrations and plasmon resonances. It affects the geometry, electron density and inter-band transition energies of the nanoparticle. Especially, the plasmon resonances frequencies depend on the sizes of the nanospheres [22]. New detection techniques have been built on plasmon frequency shifts [23–26]. Further experiments focusing on vibrations damping [8, 14, 27] have also been made.

Most results have been obtained using continuum mechanics approach. But at nanoscale, small-scale effects cannot be ignored. The vibrational properties of the nanostructures must be predicted using an appropriate approach. The modeling of the nanoparticles must incorporate the small size effect on the physical properties of nanostructures. Therefore, Ghavanloo and Fazlzadeh [28] studied the small size effect on the radial vibration of nanospheres using only nonlocal elasticity. We must consider simultaneously the strain gradient theory in order to quantify the influence of small size on the vibration frequency of nanospheres. Indeed, nonlocal and strain gradient parameters play an important role in observing the hardening and softening phenomena in nanosphere stiffness.

Motivated by this idea, a nonlocal strain gradient model is used here to study the radial vibration of isotropic nanospheres. In this way, the classical gradient model and the Eringen's nonlocal elasticity model [29, 30] are employed to fix the classical model. A governing equation of the radial vibration of isotropic nanospheres in terms of displacement potential is derived. It must be pointed that the radial vibration mode associated with dilatation is an axisymmetric mode, which has been observed in the Raman spectroscopy [31, 32]. In addition, this mode can serve as a nanoparticle fingerprint, and its frequency is crucial to characterize the nanoparticle in the Raman spectroscopy. Frequency equation of radial vibration is obtained by imposing the stress-free boundary condition. To prove the accuracy of this analysis, the numerical results are compared with the literature in certain specific cases. Finally, the effect of nonlocal and strain gradient parameters on the vibration frequency is examined in detail.

Furthermore, size effect is very significant also in functional gradient materials [33–38] which are classified as novel composite materials used in the micro- and nano-electro-mechanical systems, atomic force microscopes and thin films. For more description, there are excellent articles dedicated to the study of the size effect on the nanostructures vibration using continuum approximation [39], nonlocal elasticity theory [40], Mindlin's strain gradient theory [41] and first-order shear deformation theory [42].

2. Formulation of the isotropic nonlocal strain gradient theory

In the nonlocal strain gradient theory, the stress at any point depends on not only the strain of the whole domain V but also the higher order strain gradient. According to the nonlocal strain gradient theory proposed by Lim *et al* [43], the total stress tensor σ is expressed as follows:

$$\sigma = \sigma_0 - \nabla \cdot \sigma_1, \quad (1)$$

where σ_0 is the classical stress, σ_1 is the higher order stress tensor and ∇ is the del operator. These two stress tensors can be expressed as [43] :

$$\sigma_0(\mathbf{x}, t) = \int_V \alpha_0(|\mathbf{x} - \mathbf{x}'|, \xi_0) \mathbf{C} : \varepsilon(\mathbf{x}', t) dV' \quad (2)$$

$$\sigma_1(\mathbf{x}, t) = \zeta^2 \int_V \alpha_1(|\mathbf{x} - \mathbf{x}'|, \xi_1) \mathbf{C} : \nabla \varepsilon(\mathbf{x}', t) dV', \quad (3)$$

where α_0 and α_1 are nonlocal kernel functions proposed by Eringen [30] and that describe the nonlocal effect of the classical strain field and the strain gradient field at the point \mathbf{x}' . In these kernel functions $\xi_i = e_i b$ ($i = 0, 1$) is the nonlocal parameter introduced to consider the effect of nonlocal stress field. Also, e_0 and e_1 are the nonlocal material constants, b is the internal characteristic length and $|\mathbf{x} - \mathbf{x}'|$ is the Euclidean norm of the vector $\mathbf{x} - \mathbf{x}'$. In the constitutive equation (3), ζ is the strain gradient parameter, in other words is the material length scale parameter introduced to account for the effect of the higher order strain gradient field. In the two previous constitutive equations ε denotes the infinitesimal strain tensor at point \mathbf{x}' , \mathbf{C} is the linear isotropic fourth-order tensor of classical elasticity and \cdot denotes the double-dot product of two tensors.

In general, it is very difficult to use the integral form of constitutive equations (2) and (3). Hence, a simplified equivalent differential form of the constitutive equations is used in this study. Introducing and applying the linear differential operator $1 - \xi_i^2 \nabla^2$, ∇^2 being the Laplacian operator, to the corresponding equations (2) and (3), we get alternative expressions of the nonlocal constitutive equations in differential form [29, 30]:

$$(1 - \xi_0^2 \nabla^2) \sigma_0 = \mathbf{C} : \varepsilon \quad (4)$$

$$(1 - \xi_1^2 \nabla^2) \sigma_1 = \zeta^2 \mathbf{C} : \nabla \varepsilon. \quad (5)$$

For the sake of simplification, assuming that $\xi_0 = \xi_1 = \xi$, and combining equations (1), (4) and (5) we get the constitutive equation for the total stress in differential form [43]:

$$(1 - \xi^2 \nabla^2) \sigma = (1 - \zeta^2 \nabla^2) \mathbf{C} : \varepsilon. \quad (6)$$

Table 1. Material properties of gold and silver nanoparticles.

Material	$\rho(\text{kg m}^{-3})$	$\lambda(\text{GPa})$	$\mu(\text{GPa})$	$c_l(\text{m s}^{-1})$	$c_t(\text{m s}^{-1})$
Gold	19 283	162.980	14.730	3159.078	874.005
Silver	10 500	93.670	15.160	3436.360	1201.586

Table 2. Fundamental frequencies $\Omega(\text{cm}^{-1})$ of silver nanoparticles for different nonlocal parameters and $\zeta = 10^{-4}(\text{nm})$.

$a(\text{nm})$	Present study		Ghavanloo and Fazelzadeh [28]		Mankad <i>et al</i> [31]
	$\xi = 0(\text{nm})$	0.1 (nm)	$\xi = 0(\text{nm})$	0.1 (nm)	
1.5	36.1081	35.4210	36.0835	35.3969	34.00
1.7	31.8601	31.3851	31.8384	31.3634	34.00
2	27.0811	26.7875	27.0627	26.7691	27.60

Table 3. Fundamental frequencies $\Omega(\text{cm}^{-1})$ of gold nanoparticles for different nonlocal parameters and $\zeta = 10^{-4}(\text{nm})$.

$a(\text{nm})$	Present study		Ghavanloo and Fazelzadeh [28]		Ng and Chang [48]
	$\xi = 0(\text{nm})$	0.1(nm)	$\xi = 0(\text{nm})$	0.1(nm)	
2.9	17.5674	17.4718	17.5555	17.4596	18.39
5.75	8.8601	8.8477	8.8541	8.8415	9.37
10.1	5.0441	5.0418	5.0407	5.0384	5.37

According to this nonlocal strain gradient constitutive equation, i.e. equation (6), the nonlocal elasticity theory can be obtained by setting $\zeta = 0$ as [29, 30]:

$$(1 - \xi^2 \nabla^2) \boldsymbol{\sigma} = \mathbf{C} : \boldsymbol{\varepsilon}. \quad (7)$$

Moreover, by letting $\xi = 0$ the strain gradient theory can be obtained from equation (6) as follows [44, 45]:

$$\boldsymbol{\sigma} = (1 - \zeta^2 \nabla^2) \mathbf{C} : \boldsymbol{\varepsilon}. \quad (8)$$

To investigate the radial vibration mode of isotropic nanosphere, the general constitutive equation (6) based on the nonlocal strain gradient theory is employed hereinbelow. Moreover, unfortunately, no experiments have been conducted to predict the nonlocal parameter ξ and the strain gradient parameter ζ for the nanoparticles, we adopted $0 \leq \xi \leq 0.15 \text{ nm}$ and $0 \leq \zeta \leq 0.15 \text{ nm}$ in our investigation of the small scale effect on the radial vibration of nanospheres quantitatively.

2.1. Generalized Navier's equation

In this section, the equation of motion of an isotropic nanosphere based on the nonlocal strain gradient theory is established when the only vibration mode considered is radial. Therefore, in the absence of body forces, the dynamic behavior of an elastic nanosphere is given by the equation of motion (Newton's second law) with density constant ρ as follows:

$$\rho \frac{\partial^2 \mathbf{u}}{\partial t^2} = \nabla \cdot \boldsymbol{\sigma}, \quad (9)$$

where \mathbf{u} is the displacement vector. The equation of motion

for the nonlocal strain gradient problem can be obtained by applying the operator $(1 - \xi^2 \nabla^2)$ to the governing equation (9) and, using standard properties of tensor analysis, we get:

$$\rho(1 - \xi^2 \nabla^2) \frac{\partial^2 \mathbf{u}}{\partial t^2} = \nabla \cdot (1 - \xi^2 \nabla^2) \boldsymbol{\sigma}. \quad (10)$$

Now substituting the constitutive equation (6) in equation (10) we obtain:

$$\rho(1 - \xi^2 \nabla^2) \frac{\partial^2 \mathbf{u}}{\partial t^2} = (1 - \zeta^2 \nabla^2) \nabla \cdot (\mathbf{C} : \boldsymbol{\varepsilon}). \quad (11)$$

Finally, using the definition of the fourth order elasticity tensor \mathbf{C} and that of the infinitesimal strain tensor $\boldsymbol{\varepsilon}$, equation (11) takes the following form:

$$\begin{aligned} \rho(1 - \xi^2 \nabla^2) \frac{\partial^2 \mathbf{u}}{\partial t^2} &= (1 - \zeta^2 \nabla^2) \\ &\times [\mu \nabla^2 \mathbf{u} + (\lambda + \mu) \nabla (\nabla \cdot \mathbf{u})] \end{aligned} \quad (12)$$

in which λ and μ are the Lamé parameters. Hence, equation (12) was previously obtained by Zaera *et al* [46]. It is worth to note that by setting $\xi = \zeta = 0$, the Navier's equation for the classical elasticity theory can be obtained. Moreover, equation (12) can represent the generalized Navier's equation in the case of nonlocal strain gradient problem. Thus, equation (12) is of fourth-order in term of the displacement variable, as opposed to the Navier's equation that is of second-order.

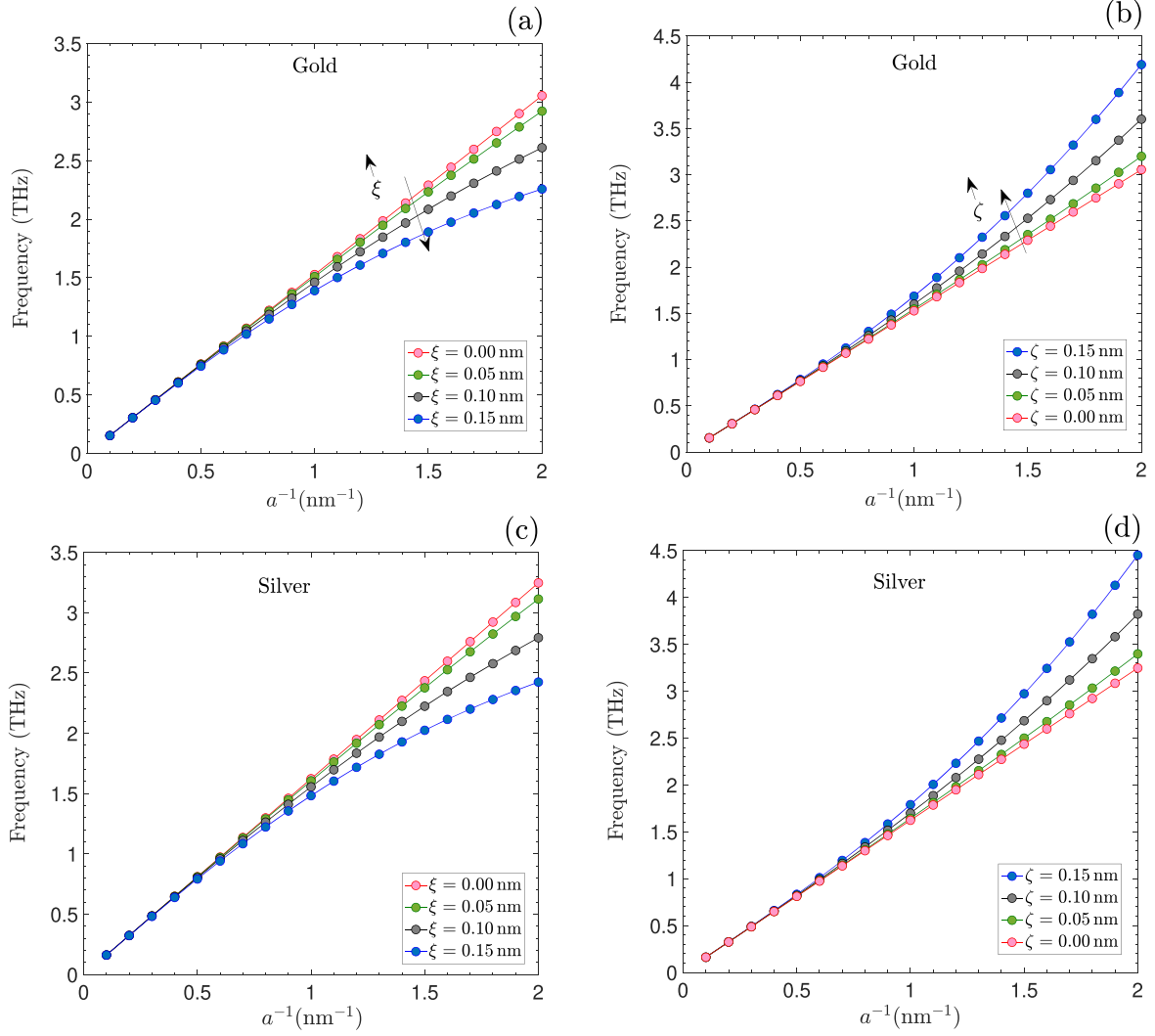


Figure 1. Fundamental frequencies as a function of a^{-1} . (a), (c) $\zeta = 10^{-4}(\text{nm})$ and (b), (d) $\xi = 10^{-4}(\text{nm})$.

3. Application to radial vibration of an isotropic nanosphere

According to the Helmholtz theorem [47], the scalar potential function ϕ for the displacement can be introduced to solve equation (12). Thus, when the only vibration mode considered is radial, the displacement vector \mathbf{u} can be written as $\mathbf{u} = \nabla\phi$. Substituting into equation (12) the generalized Navier's equation in the case of nonlocal strain gradient theory in term of scalar potential function can be obtained as follows:

$$c_l^2(1 - \zeta^2\nabla^2)\nabla^2\phi - (1 - \xi^2\nabla^2)\frac{\partial^2\phi}{\partial t^2} = 0, \quad (13)$$

in which $\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$ and $c_l = \sqrt{(\lambda + 2\mu)/\rho}$ represents the velocity of longitudinal waves in the elastic nanosphere. The vector differential equation of motion (12) is now expressed in term of the scalar potential of a much more simple form. In addition, the scalar differential equation of

motion (13) is related to the elastic perturbations that imply changes in volume.

3.1. Eigenvalue equation for the natural frequencies ω

Considering a time-periodic solutions for the radial vibration mode, the solutions of equation (13) can be assumed to the form as $\phi(r, t) = \Phi(r)e^{-j\omega t}$. Therefore, substituting this into equation (13), we can obtain a fourth order equation in terms of $\Phi(r)$ as:

$$\begin{aligned} &\zeta^2\left(\frac{d^4\Phi}{dr^4} + \frac{4}{r}\frac{d^3\Phi}{dr^3}\right) - (1 - \xi^2k_l^2) \\ &\times\left(\frac{d^2\Phi}{dr^2} + \frac{2}{r}\frac{d\Phi}{dr}\right) - k_l^2\Phi = 0, \end{aligned} \quad (14)$$

where $k_l = \omega/c_l$. The general solution to equation (14) can be written as:

$$\Phi(r) = \frac{A \sin(k_s r)}{r}, \quad (15)$$

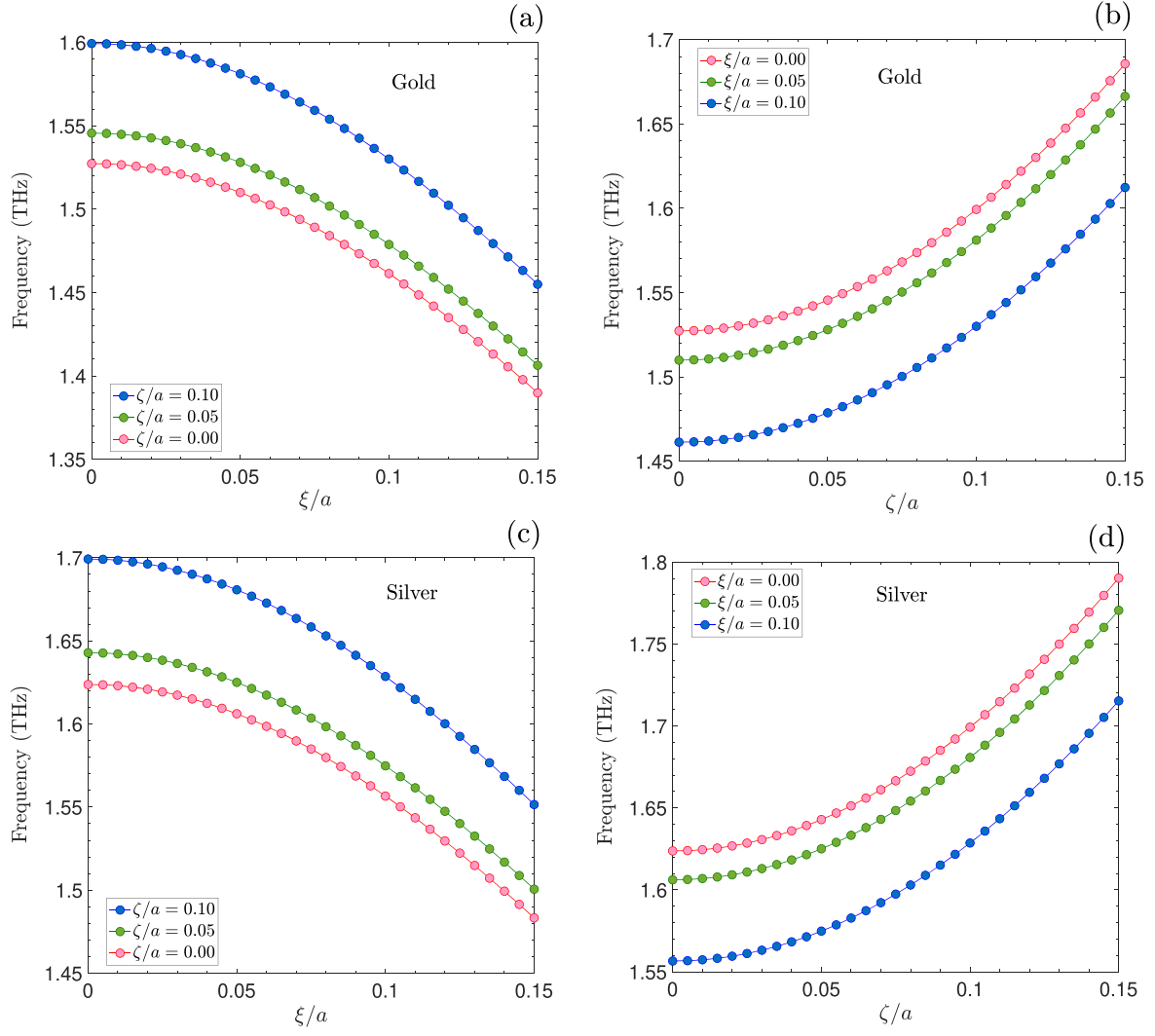


Figure 2. Variation of fundamental frequencies with respect to the (a), (c) nonlocal and (b), (d) strain gradient parameters.

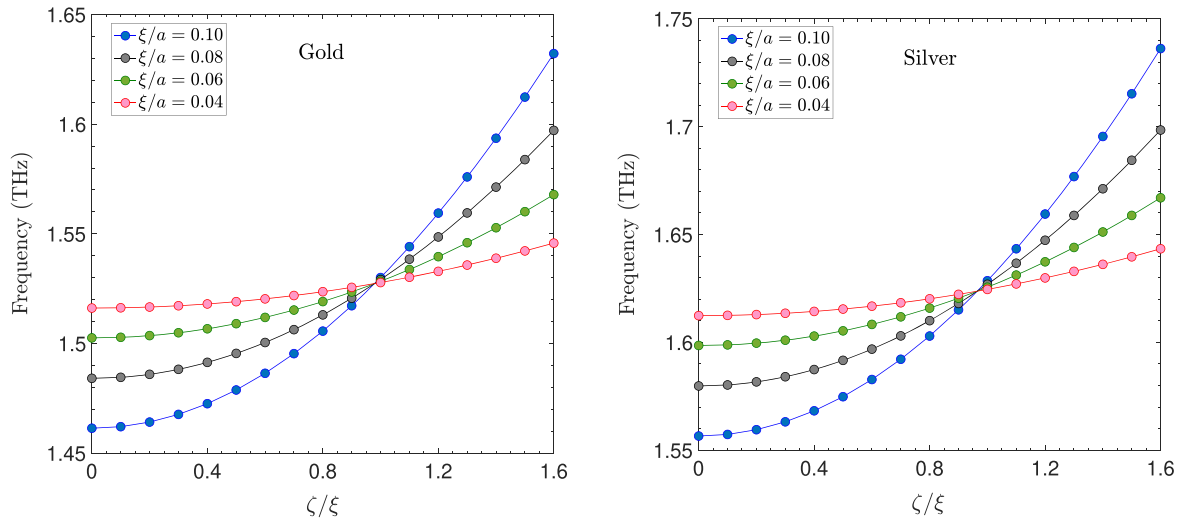


Figure 3. Variation of fundamental frequencies for different parameters of ξ/a versus ζ/ξ .

Table 4. Fundamental frequencies of the nanoparticles for different nonlocal parameters and $\zeta = 10^{-4}(\text{nm})$ (nonlocal elasticity model).

Material	Radius (nm)	Fundamental frequency $f = \frac{\omega}{2\pi}(\text{THz})$			
		$\xi = 0$ (nm)	$\xi = 0.05$ (nm)	$\xi = 0.1$ (nm)	$\xi = 0.15$ (nm)
Gold	1	1.5273	1.5099	1.4613	1.3898
	2	0.7636	0.7614	0.7549	0.7445
	3	0.5091	0.5084	0.5065	0.5033
Silver	1	1.6237	1.6061	1.5565	1.4833
	2	0.8118	0.8096	0.8030	0.7924
	3	0.5412	0.5405	0.5386	0.5353

where A is arbitrary constant and k_s can be expressed as:

$$k_s = \sqrt{\frac{\sqrt{1 + 4\beta_1\beta_2} - 1}{2\beta_1}} \quad \text{where} \quad \beta_1 = \frac{\zeta^2}{1 - \xi^2 k_l^2} \quad \text{and} \quad \beta_2 = \frac{k_l^2}{1 - \xi^2 k_l^2}. \quad (16)$$

Note that in a spherical coordinate system (r, θ, φ) located at the center of the nanosphere, the displacement field of the elastic nanosphere, $\mathbf{u} = u(r, t)\mathbf{e}_r = U(r)e^{-j\omega t}\mathbf{e}_r$, has only radial component $u(r, t)$ that is function of the distance from the origin r and time t . Using the definition $\mathbf{u} = \nabla\phi$, the radial component of the displacement field can then be obtained as:

$$U(r) = A \left[\frac{k_s \cos(k_s r)}{r} - \frac{\sin(k_s r)}{r^2} \right]. \quad (17)$$

The stress-free boundary condition, $\sigma_{rr} = 0$ at the nanosphere radius $r = a$ leads to:

$$\zeta^2 \left[(\lambda + \mu) \frac{4}{r} \frac{d^2 U}{dr^2} + (\lambda + 2\mu) \frac{d^3 U}{dr^3} \right]_{r=a} = (\lambda + 2\mu) \left[\frac{dU}{dr} \right]_{r=a} + 2\lambda \frac{U(a)}{a}. \quad (18)$$

Substituting equation (17) into boundary condition (18), the frequency equation is obtained as below:

$$\left[1 + \zeta^2 k_s^2 \left(1 - \frac{6}{k_s^2 a^2} \right) \right] \frac{k_s a}{\tan(k_s a)} + \frac{c_l^2 k_s^2 a^2}{4c_t^2} \times (1 + \zeta^2 k_s^2) + 3\zeta^2 \left(\frac{2}{a^2} - k_s^2 \right) - 1 = 0, \quad (19)$$

where $c_t = \sqrt{\mu/\rho}$ represents the velocity of transverse waves in the elastic nanosphere. Frequency equation (19) constitutes an implicit transcendental function of angular frequency ω . The roots ω may be computed for a fixed material and geometrical parameters of the nanosphere. Equation (19) was solved using Mathematica software. After finding the angular frequency, the radial vibrational frequency $f = \omega/(2\pi)$ can be calculated. It should be noted that the lowest frequency of the radial mode corresponds to a special vibrational mode, displayed by the nanoparticles, and can be observed

Table 5. Fundamental frequencies of the nanoparticles for different strain gradient parameter and $\xi = 10^{-4}(\text{nm})$ (strain gradient model).

Material	Radius (nm)	Fundamental frequency $f = \frac{\omega}{2\pi}(\text{THz})$			
		$\zeta = 0$ (nm)	$\zeta = 0.05$ (nm)	$\zeta = 0.1$ (nm)	$\zeta = 0.15$ (nm)
Gold	1	1.5273	1.5455	1.5993	1.6856
	2	0.7636	0.7659	0.7727	0.7840
	3	0.5091	0.5097	0.5118	0.5151
Silver	1	1.6237	1.6428	1.6992	1.7901
	2	0.8118	0.8142	0.8214	0.8332
	3	0.5412	0.5419	0.5440	0.5476

experimentally, and which is critical to the characterization of the nanoparticles in Raman spectroscopy.

It is easily seen from the above equation that the local or classical theory is recovered when the parameters ξ and ζ are set identically to zero. Moreover, the equation (19) becomes in this case:

$$\frac{k_l a}{\tan(k_l a)} + \frac{k_l^2 a^2}{4} \left(\frac{c_l}{c_t} \right)^2 - 1 = 0, \quad (20)$$

which was previously obtained by Lamb [20].

4. Numerical results and discussion

4.1. Comparison and validation

In order to find the radial vibration characteristics of the nanoparticles, some numerical examples are presented in this section. To determine the numerical results, basic quantities which have to be defined appropriately are the elastic constants of isotropic nanoparticles. The parameters used in this work are given in table 1 and are taken from [28].

To justify the validity of the suggested model, we compare the present results with some existing experimental and theoretical results in certain specific cases. The calculated fundamental radial frequencies of two different nanoparticles are presented in tables 2 and 3, along with the theoretical data [28] and the experimental data obtained from low frequency Raman spectra [31, 32] and molecular dynamics simulation [48]. In addition, in the theoretical study proposed by Ghanvanloo and Fazelzadeh [28], only the nonlocal elasticity theory is used, and they adopt the constitutive equation (6) to establish their frequency equation. Note that the vibrational frequencies, in m^{-1} , are introduced to achieve this comparison and are given by $\Omega = k_s c_l / (2\pi c)$ where c is the vacuum light speed. It can be seen that the results predicted by the present model are in reasonable agreement with the results reported in the literature (tables 2 and 3). Having verified the accuracy and reliability of the present model, we are now looking its application for different values of the nonlocal and strain gradient parameters.

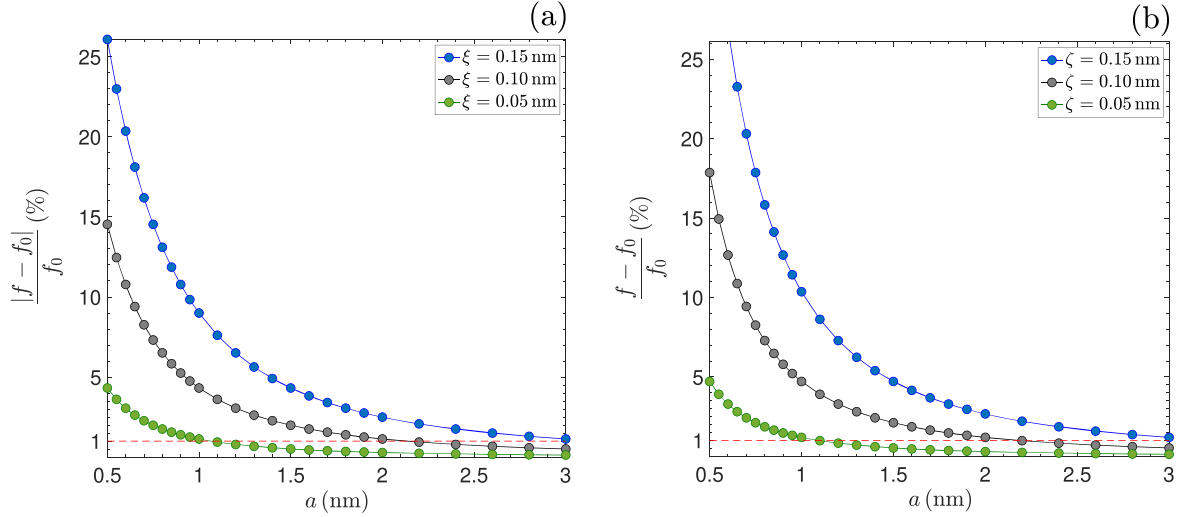


Figure 4. Relative difference versus gold nanosphere radius a . Note that f_0 corresponds to the vibration frequency for $\xi = \zeta = 0$. (a) $\zeta = 10^{-4}(\text{nm})$ and (b) $\xi = 10^{-4}(\text{nm})$.

4.2. Influence of nonlocal and strain gradient parameters on the vibration frequency

The vibration frequency of an isotropic gold and silver nanospheres as function of the inverse of radius for four values of the nonlocal and strain gradient parameters (0, 0.05, 0.10 and 0.15 nm) is plotted in figure 1.

Firstly, one can observe an important difference between the local and nonlocal strain gradient models. Figure 1 shows that when $\xi = \zeta = 0$ (local or classical theory) the frequencies are inversely proportional to the size of the nanosphere. Nevertheless, this inverse proportion relationship is considered to fail when the nanosphere radius is smaller than a critical radius, which is as a result of the small-scale effect. This critical radius depends on the relative difference between nonlocal strain gradient and local solutions of the vibration behaviors of the nanosphere that will discussed in figure 4. The second remark is the dependence of the vibration frequency versus nonlocal and strain gradient parameters. It is found from figures 1(a) and (c) that when the nonlocal parameter increases, the frequency decreases. This behavior is physically reasonable, because the nonlocal model with the small-scale effect is envisioned as atoms linked by elastic springs and makes the nanosphere more flexible, compared with the local elasticity model assuming the spring constant to take an infinite value [28]. An opposite behavior was observed in the case of strain gradient model. Figures 1(b) and 1(d) show that when the strain gradient parameter increases, the frequency increases. Furthermore, the nonlocal parameter effect on the frequency is notable for the nanospheres with very small radius. The third important comment concerns the influence of the nanosphere size. Figure 1 exhibit that the frequency highly depends on the nanosphere size and decreases with increasing size. This dependence on the nanosphere size is also highlighted in tables 4 and 5.

Figure 2 shows the effect of the non dimensional non-local and strain gradient parameters on the fundamental

natural frequency. In these figures, three values of the non dimensional nonlocal and strain gradient parameters were considered, and the effects of increasing the non dimensional nonlocal parameter (figures 2(a) and (c)) and the strain gradient parameter (figures 2(b) and (d)) were obtained. As shown in figures 2(a) and (c), with the increase in the nonlocal parameter, the frequency decreased. However, as shown in figures 2(b) and (d), the frequency increased with the increase in the strain gradient parameter. The results agreed with previous values [49], even though the vibration mechanism is fundamentally different. This emphasized the correlation that exists between the hardening and softening phenomena in nanosphere stiffness and the nonlocal and strain gradient parameters.

As mentioned above, on the nanoscale, nonlocal and strain gradient parameters play an important role in the dynamics of nanoparticles. To further clarify this issue, a number of intervals can be determined for the length scale parameter. At these intervals, the length scale parameter value can be manipulated (i.e. increased or decreased) to observe the hardening and softening phenomena in nanosphere stiffness. Figure 3 show the natural frequency changes for nanospheres and the variation of nonlocal parameter ξ/a versus variations of ζ/ξ . As depicted, generally, increasing the ζ/ξ parameter leads to increase in the natural frequency. It should be noted that when $\zeta/\xi < 1$, increasing the non-dimensional nonlocal parameter reduces the natural frequency, which leads to softening effect on the stiffness of nanosphere. In addition, when $\zeta/\xi > 1$, increasing the non-dimensional non-local parameter value causes an increase in the natural frequency, which leads to the hardening effect on the stiffness of nanosphere. These softening and hardening effects on the stiffness of nanosphere which are manifested by the decrease or increase in the vibration frequencies are also highlighted in the tables 6 and 7.

Table 6. Fundamental frequencies of gold nanoparticles for different nonlocal and strain gradient parameters with $a = 1$ nm.

	Fundamental frequency $f = \frac{\omega}{2\pi}$ (THz)			
	$\zeta = 0$ (nm)	$\zeta = 0.05$ (nm)	$\zeta = 0.1$ (nm)	$\zeta = 0.15$ (nm)
$\xi = 0$. (nm)	1.5273	1.5455	1.5993	1.6856
$\xi = 0.05$ (nm)	1.5099	1.5280	1.5811	1.6663
$\xi = 0.1$ (nm)	1.4613	1.4788	1.5300	1.6123
$\xi = 0.15$ (nm)	1.3898	1.4063	1.4549	1.5329

The relative difference between nonlocal strain gradient and local solutions of the vibration behaviors of the nanosphere is displayed in figure 4. It shows that the relative difference of the vibration frequency declines as the radius increases. Moreover, all the curves converge gradually for a sufficiently large radius. The relative difference depends on the used model (nonlocal elasticity theory or strain gradient theory). In particular, for the nanosphere with 3 nm radius and a nonlocal parameter of $\xi = \zeta = 0.15$ nm, the relative difference on the vibration frequency is 1%. On the other hand, it is also possible to determine a critical radius for obtaining a given relative difference. For example, to obtain a relative difference of 1% for the nonlocal parameter $\xi = \zeta = 0.15$ nm, it is necessary to choose a critical radius of 3 nm. In other words, if we take a radius of 3 nm, and a nonlocal parameter between 0 and 0.15 nm, the predictions of the vibration frequency based on the local elasticity model are valid for a nanosphere. The validity of the local classical elasticity theory depends on the desired relative difference. In addition, the relative difference reduces as the nonlocal parameter decreases, which is because the nonlocal effect diminishes.

5. Conclusion

A new accurate, simple formulation based on nonlocal strain gradient theory in order to predict the radial vibration of isotropic nanospheres which can handle the small size effect is developed in this paper. The main novelty of the present article was to develop an applicable model to obtain a better insight into vibrational properties of the isotropic nanospheres with consideration of the small scale effect. The obtained results have been successfully compared to experimental and theoretical results for gold and silver nanospheres. The numerical results revealed that the inverse proportion relationship between the frequency and the nanosphere radius was deemed to fail when the radius is smaller than a critical radius which depends in to the desired relative difference, where the small-scale effects cannot be disregarded. Moreover, it was observed that the hardening and softening phenomena in nanosphere stiffness greatly depend on the ratio between the nonlocal and strain gradient parameters ζ/ξ .

Generally, the physical behavior and vibrational properties of the isotropic nanoparticles can be described by a classical elasticity theory ($\xi = \zeta = 0$), which predicts an

Table 7. Fundamental frequencies of gold nanoparticles for different nonlocal and strain gradient parameters with $a = 1.5$ nm.

	Fundamental frequency $f = \frac{\omega}{2\pi}$ (THz)			
	$\zeta = 0$ (nm)	$\zeta = 0.05$ (nm)	$\zeta = 0.1$ (nm)	$\zeta = 0.15$ (nm)
$\xi = 0$ (nm)	1.0182	1.0236	1.0397	1.0662
$\xi = 0.05$ (nm)	1.0130	1.0184	1.0344	1.0607
$\xi = 0.1$ (nm)	0.9979	1.0032	1.0190	1.0449
$\xi = 0.15$ (nm)	0.9742	0.9794	0.9948	1.0200

inverse proportion relationship between the vibrational frequencies and the nanospheres size. An important contribution of this paper is the analysis of the impact of both nonlocal parameter ξ (i.e. nonlocal elasticity effect) and the strain gradient parameter ζ (i.e. strain gradient effect) on the vibrational properties of the nanospheres. These properties are original and can be particularly useful in the characterizing nanoparticles shape, size, and size distribution. From the performed analysis and numerical calculations, one can conclude that:

- An important difference between the local and nonlocal strain gradient models has been observed. When $\xi = \zeta = 0$ (local theory) the frequencies are inversely proportional to the size of the nanosphere. Nevertheless, this inverse proportion relationship is considered to fail when the nanosphere radius is smaller than a critical radius, which is as a result of the small-scale effect. This critical radius depends on the relative difference between nonlocal strain gradient and local solutions of the vibration behaviors of the nanosphere.
- A significant dependence of the vibration frequency versus nonlocal and strain gradient parameters has been highlighted. When the nonlocal parameter increases, the frequency decreases. This behavior is physically reasonable, because the nonlocal model with the small-scale effect is envisioned as atoms linked by elastic springs and makes the nanosphere more flexible, compared with the local elasticity model assuming the spring constant to take an infinite value. An opposite behavior was observed in the case of strain gradient model. When the strain gradient parameter increases, the frequency increases. Furthermore, the nonlocal parameter effect on the frequency is notable for the nanospheres with very small radius.
- The vibrational frequency is highly depends on the nanosphere size and decreases with increasing size.
- With the increase in the nonlocal parameter ξ , the vibrational frequency decreased. However, the vibrational frequency increased with the increase in the strain gradient parameter ζ . This emphasized the correlation that exists between the hardening and softening phenomena in nanosphere stiffness and the nonlocal and strain gradient parameters.

- When the ratio between the strain gradient parameter and the nonlocal parameter is less than 1 ($\zeta/\xi < 1$), increasing the non-dimensional nonlocal parameter value ξ/a reduces the natural frequency, which leads to softening effect on the stiffness of nanosphere.
- When $\zeta/\xi > 1$, increasing the non-dimensional nonlocal parameter value causes an increase in the natural frequency, which leads to the hardening effect on the stiffness of nanosphere.
- The validity of the classical elasticity theory depends on the desired relative difference. This relative difference reduces as the nonlocal parameter decreases, which is because the nonlocal effect diminishes. For example, if we take a radius of 3 nm, and the nonlocal and strain gradient parameters between 0 and 0.15 nm, the predictions of the vibration frequency based on the classical elasticity theory are valid for a nanosphere.

This work is original contribution to the state of the art. Since it covers the small-scale effect on the free vibration of nanospheres, the results obtained can be used to characterize nanoparticles shape, size, and size distribution. Thus, the obtained generalized frequency equation for radial vibration is very useful to interpret the experimental measurements of vibrational characteristics of nanospheres.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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