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A finite-size statistical mechanics approach to quantum confinement effects on nanoscale energy-related properties

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The effects of quantum confinement on the energy-related properties of nanoscale materials and structures are critical for understanding their electronic, optical, and thermal behaviors. This study investigates these effects through a finite-size statistical mechanics framework, integrating theoretical analysis with experimental validation. By examining key material systems, this work provides insights into the mechanisms governing energy-related behaviors at the nanoscale, with implications for advanced applications in energy storage, conversion, and photonics.

I. Introduction

This communication explores the influence of quantum confinement on the energy properties of nanoscale materials and structures. Quantum confinement is a phenomenon that occurs when a material's dimensions are reduced to a few nanometers, approaching, for instance, the de Broglie wavelength of its electrons or the exciton radius. At this scale, the system becomes 'trapped', resulting in quantized energy levels akin to those in a potential well. This quantization profoundly alters the material's electronic and optical properties, as observed in quantum dots, nanowires, and thin films, see for instance ref. 1,2. Additionally, quantum confinement impacts the thermal properties of these materials by modifying the behavior of confined phonons and their interactions with electrons, excitons, plasmons and other quasi-particles, thereby influencing heat conduction, thermal emission and thermal management. It also extends to photons in nanocavities, where a strong spatial confinement of electromagnetic waves alters their interaction with matter with respect to the far field blackbody limit of macroscopic bodies, to cite a well-known system.^{2–5} These effects of quantum confinement are

New concepts

Finite-size statistical mechanics (FSSM), a novel theory, is a groundbreaking framework that revolutionizes our understanding of nanomaterials by directly addressing finite-size and confinement effects. Its core insight comes from recognizing that statistical mechanics remains invariant when energy and temperature are simultaneously rescaled. This robust and validated framework proves valuable for explaining and predicting the energy-related behaviors of nanoscale materials. It particularly addresses a major nanoscience challenge: how the density of vibrational states in nanomaterials deviates significantly from the Debye model due to their size. FSSM elegantly resolves this by demonstrating that the Debye density can be recovered through the introduction of rescaled frequency and temperature, effectively accounting for these size effects. By providing deep mechanistic insights into how quantum confinement dictates electronic, optical, and thermal properties, FSSM moves beyond observation to explain the underlying physics. This fundamental understanding, coupled with experimental validation, is crucial for developing advanced applications in energy storage, conversion, and photonics, paving the way for next-generation technologies.

pivotal to many modern scientific advancements, as indicated in the references.

One of the notable observations in quantum confined systems is the fact that the density of vibrational states is greatly affected by the nanometric length of the system and no longer adheres to the Debye model.^{3,6,7} Nonetheless, the use of the Debye density can be recovered by introducing both a rescaled frequency and temperature that account for size effects in the quantum statistical mechanics description, as will be described below. This rescaling is done by leveraging the invariance of statistical mechanics, in particular, of the fundamental Boltzmann factor under re-scaling of the energy-to-temperature ratio. This represents our original contribution.

The structure of this communication is as follows: Section 2 introduces our concept of thermal scaling. Section 3 examines the radiative heat transfer problem between two bodies, considering both the near field and the far field. Section 4 focuses on determining the temperature dependence of the bandgap in nanoscale semiconductors. Finally, Section 5 presents our conclusions.

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II. Thermal scaling and quantum confinement

Adopting a modified density of vibrational modes is not the only theoretical way to account for the anomalies in the optoelectronics and the thermal properties reported for nanostructures and materials.^{1,2,4,5} In fact, by appropriately rescaling both the energy and temperature of systems, the statistical mechanics framework remains consistent, offering a powerful tool for analyzing these properties.

This consistency comes from the fact that the probability of a system being in a certain state is given by the Boltzmann distribution,

$$P \sim \exp(-E/k_{\text{B}}T), \quad (1)$$

where E is the energy of the state, k_{B} is the Boltzmann constant, and T is the temperature. This particular dependence on the energy-to-temperature ratio $\varepsilon = E/k_{\text{B}}T$ makes the statistical mechanics an invariant theory under simultaneous rescaling of both energy and temperature and can lead to equivalent descriptions that retain the same statistical properties. This approach helps in identifying universal behaviors and critical phenomena in different materials at the nanoscale.

Recalling the dynamics of electrons, it is known that when the dimensions of the confining structure decrease, the energy spacing between the discrete levels characterizing its energy spectra usually increases.⁸ Hence, because of the Heisenberg uncertainty principle, a strongly confining region thus, implies a broader kinetic energy range. This increase in the kinetic energy range naturally reflects in an increased temperature of the system. This fact suggests that the mechanical statistical description of the highly confined system should account for increments in both energy and temperature, such that the following scaling relation is valid.^{9,10}

$$\frac{\hat{E}}{k_{\text{B}}\theta} = \frac{E}{k_{\text{B}}T}, \quad (2)$$

Here, \hat{E} is the energy of a bulk system at the rescaled temperature θ , while E represents the directly measurable energy of the actual system. Notice that the increase of energy levels and of temperature should depend on the characteristic length of confinement, l and, therefore, can be interpreted as an entropic constriction, as discussed in ref. 9.

Thus, the thermal energy is now characterized by the parameter $\theta(l)$, which is an apparent or effective temperature that may depend on the structure and symmetry of the system,¹⁰ under the boundary conditions^{9,11} or even in external forces.¹² Therefore, the selection of the adequate thermal parameter determines the corresponding statistics.

The ratio of \hat{E} and the rescaled temperature θ can be expressed as follows (see ref. 9,13–17):

$$\frac{\hat{E}}{k_{\text{B}}\theta} = \frac{\hat{E} - m^*\mu}{k_{\text{B}}T}, \quad (3)$$

which, in view of eqn (2), yields the relation

$$\hat{E} - m^*\mu = E, \quad (4)$$

where m^* represents an effective mass and μ denotes the chemical potential. Rescaling is akin to introducing a chemical potential μ , such that E corresponds to the energy adjusted for the confinement effects dictated by this chemical potential.

Reinterpreting eqn (4) in terms of frequencies as

$$h\hat{\nu} - m^*\mu = E, \quad (5)$$

reveals that the chemical potential induces a shift in the frequencies, which in turn reorganizes the material's energy structure and alters its optoelectronic, thermal, and mechanical properties, with a more significant impact at the nanoscale compared to the bulk form.

At this stage, guidelines for determining the effective temperature θ are needed. In cases of light emission and absorption involving nanocrystals,^{9,10,18} Wien's displacement law helps determine the effective temperature

$$\theta = \frac{C_{\text{W}}}{l}, \quad (6)$$

where C_{W} is the Wien's constant and l is the characteristic nanoscopic length associated with the confinement.

On the other hand, with regard to the thermal properties of nanocrystals, an explicit relation between T and θ can be established by comparing the dispersion relations for the Debye frequencies of a bulk crystal and nanocrystal, $\hat{\nu}_{\text{D}}$ and ν_{D} , respectively, given as $\hat{\nu}_{\text{D}} = \hat{c}_{\text{s}}\hat{k}_{\text{D}}$ and $\nu_{\text{D}} = c_{\text{s}}k_{\text{D}}$, where \hat{c}_{s} and c_{s} are the Debye velocities, and \hat{k}_{D} and k_{D} are the Debye wave numbers for the nanocrystal and bulk crystal, respectively. These wave numbers are linked to the size of the characteristic domains in each system, leading to the relations $\hat{k}_{\text{D}} \sim 1/\hat{l}$, where \hat{l} is the lattice constant, and $k_{\text{D}} \sim 1/l$, where l is a characteristic length corresponding to the size of the nanocrystal. From this, it follows that $\hat{\nu}_{\text{D}}/\nu_{\text{D}} \sim l/\hat{l}$. When expressed in terms of temperatures, the relationship becomes $\theta_{\text{D}}/T_{\text{D}} \sim l/\hat{l}$. Assuming the proportionality holds true at all temperatures, $\theta/T \sim l/\hat{l}$. Consequently, the effective temperature of a nanocrystal is proportional to its size.

The role of these confinement lengths reflecting an asymmetry or anisotropy in the system, either geometrical or related to microscopic interactions, has been previously studied from a fundamental point of view in ref. 19, but, as far as we know, was not incorporated in the statistical mechanics framework until recently. In the referred work it is emphasized that molecules and atoms in molecules are not isotropic, and then it is discussed that how anisotropic atom–atom potentials improve the quantitative understanding of particular polyatomic systems. These improvements come from anisotropies in the local charge distribution and to anisotropies in the repulsive wall around the atom. However, beyond the microscopic analysis of the interactions, including corrections using multipole expansion contributions,^{19–21} the authors conclude that several features of the pair interaction potentials can be understood in terms of simple ideas such as classical electrostatics and molecular shapes.



III. Radiative heat transfer in both the near field and far field

In recent years, a revolutionary series of near field radiation studies have been published in which the radiative heat exchange involving nanogaps of about $1\text{--}10^2$ nm has tackled the nature of the matter–radiation interaction under non-equilibrium conditions, see for instance ref. 4 and 5. In the far field case, the emission of radiation from nearly 2D nanoscale flakes has been reported in ref. 1 and 2 emphasizing the asymmetry of the confinement and the dependence of the emitted radiation on confinement lengths of about 10^2 nm.

Under thermal rescaling, Planck's law for the density of thermal radiation can be maintained and remains unchanged. Consequently, the rescaled form of Planck's law is given by

$$\hat{u}(\hat{\nu}) = \frac{8\pi\hat{\nu}^2}{c^3} \frac{h\hat{\nu}}{\exp\left(\frac{h\hat{\nu}}{k_B\theta}\right) - 1}, \quad (7)$$

where the factor $\frac{8\pi\hat{\nu}^2}{c^3}$ corresponds to the Debye spectral density.

In this context, eqn (7) represents the spectral energy density of a blackbody (BB) at a given temperature θ . By using eqn (3) we can rewrite eqn (7) in terms of the chemical potential μ

$$\hat{u}(\hat{\nu}) = \frac{8\pi\hat{\nu}^2}{c^3} \frac{h\hat{\nu}}{\exp\left(\frac{h\hat{\nu} - m^*\mu}{k_B T}\right) - 1}, \quad (8)$$

which, as known in the literature, although in a different context, represents the generalized Planck's law.^{9,13–17}

A. Near field: equilibrium and non-equilibrium

Now, turning to eqn (2), this becomes even more intriguing when applied to photons in a cavity:

$$E = h\hat{\nu}\frac{T}{\theta} = h\hat{\nu}\frac{T}{C_W}l \quad (9)$$

revealing that the energy per photon is adjusted based on the confinement length. The potential of the previous equation lies in the fact that it allows us to calculate the work ΔF required to confine the radiation in a cavity of volume V at a temperature T as follows

$$\Delta F = \frac{VT}{\theta} \int_0^\infty \hat{u}(\hat{\nu}) d\hat{\nu}. \quad (10)$$

As a noteworthy outcome, eqn (10) enables us to derive the pressure:⁹

$$p = -(\partial F / \partial V)_T \sim \frac{k_B T}{l^3}. \quad (11)$$

Omitting the prefactors, this constitutes the thermal correction to the Casimir effect, where V is assumed to be the volume of a nanocavity with a constant cross-section and a variable width l .

Another application of our approach involves a non-equilibrium effect: heat exchange between two flat plates with

temperatures $T_1 < T_2$,⁹ which can be described through the energy current between the plates, defined as

$$\dot{Q} = \frac{(\Delta F)_2 - (\Delta F)_1}{\tau}. \quad (12)$$

Here, τ is a timescale which, based on an educated guess informed by quantum principles, we infer should behave as the inverse of the plasma frequency ω_p : $\tau \sim (N_a \omega_p)^{-1}$, where N_a is the Avogadro number. Using eqn (10) and expanding eqn (12) to first order in the temperature difference, $\Delta T = T_2 - T_1$, give

$$\dot{Q} \sim -G\Delta T, \quad (13)$$

where

$$G \sim \frac{\tau^{-1}}{l^2}, \quad (14)$$

is, except for prefactors, the thermal conductance, with the l^{-2} dependence commonly observed in experiments.

However, unlike metals, for which the previous relation holds at any distance, this is not true for insulators. According to band theory, insulating materials can behave as conductors at very high temperatures. Within our approach, high temperatures θ correspond to very short distances. Henceforth, the frequency density must be adjusted by a form function $f(l)$ such that

$$\rho(\hat{\nu}) = \rho_D(\hat{\nu})f(l), \quad (15)$$

where $\rho_D(\hat{\nu})$ is the Debye spectral density. Consequently, the thermal conductance must be adjusted by $f(l)$ so that

$$G = G_m f(l), \quad (16)$$

where G_m is given by eqn (14). The crossover behavior from $1/l$ for large gaps to $1/l^2$ for very narrow gaps is derived by performing a first-order expansion of the form function $f(l) = 1 + l/l_c$, with l_c representing the crossover distance.⁹

B. Far field

In the far-field case,¹⁰ the length scale introduced by the Wien law is determined by the physical dimensions of the body itself. Hence, to address the issue of energy exchange in the far field, we begin by considering the irradiance of a nanocrystal.

The energy irradiated $I(\nu)$, per frequency band, by a small body is given by the following relation $d_\nu I = c\alpha(\nu)u(\nu)d\nu$, where c is the speed of light in vacuum and $\alpha(\nu)$ is the absorption cross-section.²² For a nanocrystal with volume V , the previous relationship can be expressed as follows:

$$d_\nu I = \frac{1}{\tau} V \frac{T}{\theta} \hat{u}(\hat{\nu}) d\hat{\nu}. \quad (17)$$

After multiplying and dividing by a factor of $4c$, eqn (17) can be compared to the well-known spectroscopic expression²³ for the absorption cross-section, allowing us to identify

$$\hat{\alpha}(\hat{\nu}) = \frac{4VT}{\tau c \theta}. \quad (18)$$

Similarly, in molecular spectroscopy, it is understood that the absorption cross-section depends on the frequency through



the spectral lineshape $g(\hat{\nu})$. Thus, unlike the case of near-field radiation in a vacuum cavity, we must define the characteristic time-scale here as $\tau^{-1} = \hat{\nu}g(\hat{\nu})$.

As a result of the dependence of the optoelectronic properties on temperature, we assume that

$$g(\hat{\nu}) = f(T)\tilde{g}(\hat{\nu}), \quad (19)$$

where $f(T)$ can be roughly described by the maximum contribution of the Doppler effect

$$f(T) \sim \left(\frac{m_{\text{eff}}c^2}{2k_{\text{B}}T\hat{\nu}_{\text{res}}^2} \right)^{1/2}. \quad (20)$$

Here, m_{eff} is the effective mass, and $\hat{\nu}_{\text{res}}$ is the resonant frequency.

Conversely, the classical approach assumes that the spectral lineshape corresponds to the imaginary component of the Cole–Cole susceptibility function^{23,24}

$$\tilde{g}(\hat{\nu}) = \frac{(\tau_{\text{res}}\hat{\nu})^\delta \sin(\pi\delta/2)}{1 + 2(\tau_{\text{res}}\hat{\nu})^\delta \cos(\pi\delta/2) + (\tau_{\text{res}}\hat{\nu})^{2\delta}}. \quad (21)$$

Here, δ is the characteristic exponent of the relaxation process and τ_{res} is the time at which the maximum of the absorption function occurs. Additionally, notice that when $\delta < 1$ we have the classical response behavior associated with the Cole–Cole function.²⁴ Alternatively, for $\delta > 1$, the response becomes enhanced.

With this background, for $T/\theta < 1$ and adopting $\tau_{\text{res}}^{-1} \simeq k_{\text{B}}T/h$ as the physically meaningful simple assumption we achieve¹⁰

$$\frac{I_\delta(T, l)}{\sigma T^4} = B_\delta \frac{k_{\text{B}}T}{hc} \sqrt{\frac{1}{T^3}} \sin\left(\frac{\pi\delta}{2}\right) \left(\frac{C_{\text{W}}}{Tl}\right)^{4-\delta} V, \quad (22)$$

where σ denotes the Stefan–Boltzmann constant. Furthermore, to simplify the equation and reduce notational complexity, we have defined the constant $B_\delta \equiv (60/\pi^4)\Gamma(5-\delta)\zeta(5-\delta)\phi$, where $\phi = [m_{\text{eff}}c^2h^2/(2k_{\text{B}}^3)]^{1/2}$ and $\zeta(x)$ represents the Riemann zeta function.

Thus, using eqn (22), we can determine the heat conduction between two anisotropic bodies at different temperatures ($T_1 < T_2$), which is experimentally verifiable.¹⁰ Similar to the near-field case, we computed the heat current \dot{Q} and, from this, determined the heat conductance $G_\delta(l)$, incorporating cooperative effects

$$G_\delta = 4F_{1,2} \frac{V}{l} \left[1 + \sin\left(\frac{\pi\delta}{2}\right) \frac{k_{\text{B}}B_\delta}{hc} \frac{1}{T^2} \frac{(\lambda_T)^{4-\delta}}{l^{3-\delta}} \right] \sigma T^3. \quad (23)$$

In this context, it is important to follow the established conventions in the field to introduce the view factor $F_{1,2}(l/d)$,²⁵ a parameter that depends on the ratio of the characteristic length to the separation between the bodies, d , under the condition $d \gg \lambda_T$, where λ_T is the Wien length at temperature T .

IV. Temperature dependence of the bandgap in nanoscale semiconductors

In this section, we illustrate how the previously introduced theory can be utilized to explain the optoelectronic properties of nanomaterials.¹⁸ In particular, we will focus on the effects that strong quantum confinement has on the optical band-gap energy and that have been observed in the photoluminescence emission of 2D and 2D-layered materials (ref. 26 and 27) as well as in CsPbBr₃ nanocrystals.^{28,29} Some of these effects have been confirmed by *ab initio* simulations,³⁰ showing them to correspond to black phosphorene flakes having sub-nanometer widths for a single layer to 46 nm in the multilayer case.

The key point here is the unusual temperature dependence of the optical bandgap energy, which, in contrast to bulk systems, increases with temperature or exhibits a non-monotonic behavior characterized by a blue-shift and red-shift pattern.

The optical bandgap energy can be determined from photoluminescence experiments by identifying the peak position in the photoluminescence spectrum. Following our approach, this corresponds to the energy difference between two states in the conduction and valence bands, $\Delta E_{\text{g}} = E_{\text{c}} - E_{\text{v}} \equiv h\nu_{\text{g}}$

$$\Delta E_{\text{g}} = \frac{T}{\theta} h\nu_{\text{g}} = \frac{T}{\theta} \frac{hc}{d_{\text{p}}}, \quad (24)$$

where we have used the relation $\hat{\nu}_{\text{g}} = c/d_{\text{p}}$. Here, we define d_{p} as the effective length of the electric dipole associated with the generation of electron–hole pairs and excitons, which is also linked to the Bohr exciton radius.

A. Monotonic behavior

Monotonic behavior is observed in multi-layer two-dimensional semiconductors. For these systems the transient dipole length should be related to the average layer width, $d_{\text{p}} = \kappa N\bar{l}(T)$, where κ is a proportionality constant and N is the number of layers.

Determining the average layer width, $\bar{l}(T)$, necessitates a microscopic model. In this framework, $\bar{l}(T)$ is linked to the deformation relative to the layer width at the minimum experimental temperature, l_0 , denoted as $u = l(T) - l_0$. This deformation arises from a linear chain of atoms interacting anharmonically through a Morse potential³¹

$$V(u) = D[1 - e^{-au}]^2. \quad (25)$$

For this potential, the average system deformation can be expressed in terms of the vibrational temperature of phonons $T_{\text{v}} = h\nu_{\text{phon}}/k_{\text{B}}$, which is associated with a characteristic frequency ν_{phon} :

$$\bar{u} = 3ba^{-1} \frac{\bar{E}(T)}{k_{\text{B}}T_{\text{v}}}. \quad (26)$$

Here, $b = k_{\text{B}}T_{\text{v}}/(4D)$ represents the degree of anharmonicity inherent in the Morse interaction. This parameter is expressed as the ratio of the vibrational energy $k_{\text{B}}T_{\text{v}}$ to the interatomic interaction strength D . Additionally, a^{-1} denotes the range of



the interatomic potential. A higher vibrational energy corresponds to greater anharmonicity and an increased value of b . Thus, the term $3ba^{-1}$ serves as a measure of the range of the potential while accounting for its anharmonicity. Finally, at the lowest order in energy contribution, $\bar{E}(T)$ can be taken as the average internal energy of a harmonic oscillator, that is

$$\bar{E}(T) = \frac{k_B T_v}{e^{\frac{T_v}{T}} - 1} \quad (27)$$

Notice however that the deformation of the material depends crucially on the anharmonicity of the Morse potential through the parameter b , defined above. The incorporation of the average harmonic energy at this level may restrict the application range of this formula to not too high temperatures. However, it seems to work well up to room temperatures.¹⁸ From the two preceding equations, we can deduce the explicit expression for the averaged layer width as

$$\bar{l}(T) = l_0 \left\{ 1 + \frac{3ba^{-1}}{l_0} \frac{1}{e^{\frac{T_v}{T}} - 1} \right\} \quad (28)$$

Therefore, by applying this last equation to the definition of d_p and using eqn (24) we find the desired result for the gap energy:

$$E_g = E_{g,0} + \frac{hc}{C_w} \frac{1}{\kappa N} \frac{T}{1 + \frac{\lambda}{e^{\frac{T_v}{T}} - 1}} \quad (29)$$

where we have defined the length ratio $\lambda = 3ba^{-1}/l_0$, which compares the effective range of the potential, $3ba^{-1}$, to the characteristic length of the material (such as the width in the case of 2-D materials), l_0 , at the minimum experimental temperature T_0 . In this context, $E_{g,0}$ denotes the reference energy at the temperature T_0 .

For 2-D materials, it is reasonable to assume that $3ba^{-1} \lesssim l_0$, which suggests that the term

$$\frac{\lambda}{e^{\frac{T_v}{T}} - 1} \quad (30)$$

in eqn (29) can have a significant impact.

We emphasize that eqn (29) captures the dependence of the bandgap energy on both the number of layers and temperature, specifically predicting a monotonic increase as the temperature rises. The experimental test is discussed in ref. 15.

B. Non-monotonic behavior

In contrast to the 2-D materials discussed above, experimental observations show that the bandgap energy of 3-D nanocrystals displays non-monotonic behavior with increasing temperature, displaying both blueshift and redshift. This non-monotonic behavior is also described in eqn (29). Specifically, for the case where $\lambda \lesssim 1$, the range of the interatomic potential may be smaller than the characteristic length. In this case, the term in eqn (30) can be treated as a small parameter, enabling an expansion of eqn (29) in terms of this small parameter. Expanding to the first order, the energy gap can be represented by the

following relation:

$$E_g = E_{g,0} + \frac{hc}{C_w} \frac{1}{\kappa^*} T \left(1 - \frac{\delta}{e^{\frac{T_v^*}{T}} - 1} \right) \quad (31)$$

In eqn (31), we have redefined the set of parameters as κ^* , δ and T_v^* to distinguish them from their counterparts κ , λ and T_v in eqn (29), as both eqn (29) and (31) describe systems with different characteristics. The experimental validation of our result, as described by eqn (31), is provided in ref.18.

V. Conclusions

In this communication, we have introduced a novel theory, finite-size statistical mechanics, capable of revealing the underlying effects of quantum confinement on the thermal and optoelectronic properties of nanomaterials. The core of our theory lies in exploiting the invariance of a statistical mechanics description under the rescaling of energy and temperature allowing one to incorporate finite-size and confinement effects. Although the theory is formulated for equilibrium situations, it is worth noting that it may also be used to determine finite-size effects in transport coefficients under non-equilibrium conditions, such as in the case of heat exchange in nanocavities, as discussed in Section IIIA.

Extensions of this approach to soft-matter systems far from thermodynamic equilibrium have been explored in previous works,^{32–35} among others. Similarly, recent advancements in hybrid methodologies that incorporate DFT, molecular dynamics, and finite element simulations^{36,37} have improved the molecular dynamics description of charge transport processes in confined structures at a molecular level by incorporating finite-size, anisotropic, and non-periodic electric fields. These theoretical efforts, which focus on developing more precise molecular dynamics simulations, share a view of statistical mechanics that is similar to ours; yet, they adopt a complementary bottom-up perspective.

As demonstrated in our previous publications,^{9,10,18} our theory offers a robust framework capable of accurately describing a range of experimental findings. This framework effectively accounts for phenomena such as near- and far-field radiative energy transfer and the photoluminescence measurement of optical bandgap energy in 2D nano-semiconductors, requiring at most two free parameters.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data that support the findings of this study are available from the corresponding author agustiperezmadrid@ub.edu upon reasonable request.



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