

DECAY OF MESOSCOPICALLY LOCALIZED VIBRATIONS IN POROUS MATERIALS

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The low temperature decay of a vibrational eigenstate of a crystalline mesoscopic particle surrounded by other such particles of approximately the same size is considered. The decay time is determined by the anharmonicity and the coupling between adjacent mesoscopic particles. Under some limiting conditions for particles of a typical size of 50 Å the decay time at low temperatures can be several ms.

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In a recent paper by Kaplyanskii, Feofilov and Zakharchenya [1] long-lived size-quantized vibrational states in porous Al₂O₃ were studied at low temperatures between 2 and 5 K. Non-equilibrium phonons were excited by “optical heating” with a laser pulse. The anti-Stokes spectrum was observed at long time delays of 2 — 4 ms and a low-frequency maximum at $\omega_0 \approx 20 \text{ cm}^{-1}$ was found to decay for ~ 1 ms. The purpose of the present Letter is to provide a theory of the decay rate of such vibrational states which might shed light on the origin of the exceptionally large decay times observed in the experiment.

The physics of the phenomenon can be described as follows. The sample of Al₂O₃ consists of particles of approximately (but not exactly) the same size of about 50 Å diameter which are presumably only weakly connected, i.e. most of the bonds on the surface of a particle are dangling. Some of the particles might constitute “dead ends”, others can be connected with several neighbors but still most of the particles’ surface can be considered as free.

Due to the small dispersion of the mesoscopic crystal sizes and the comparatively large density our system is distinct from typical aerogels [2]. In these the typical lengths may vary by some orders of magnitude, leading to fractal behavior [3]. It is equally distinct from a glass [4]. There one has only one length scale, the atomic one.

We consider porous materials where two length scales exist. Additionally to the microscopic scale of the inter-atomic distance, the nanocrystal size provides a second, a mesoscopic scale. We insinuate that the novel type of solids investigated in [1] belongs to this type. We assume that there is near to perfect order inside the single particles on atomic scales. On the mesoscopic scale, we envisage the material to be built from the single crystalline particles. The comparatively large density and the small variation of the particle sizes will ensure some inter-particle short range order. One should not expect any long range order.

Corresponding to this structure we expect two types of vibrations. The intra particle vibrations are determined by the inter-atomic forces and their wavelengths are limited by

the particle size. In first approximation these states are given by the isolated particles with free surface boundary conditions. We will provide an algorithm for the calculation of the lifetimes of lowest frequency modes. These can indeed be very large. Additionally to these modes there are inter-particle vibrations whose wavelengths are larger than the typical particle size and whose frequencies are determined by the much weaker inter-particle coupling. Both types of vibrations interact. The strength of the interaction is proportional to the ratio between inter-particle and inter-atomic coupling. We consider the case where this is sufficiently small.

The material is characterized by a narrow distribution of the particle diameters. We further assume a coupling between the crystallites so weak that there is a gap between the respective spectra of the intra and inter particle vibrations. The average density is in the range of 30% to 50% of the crystalline one and the typical diameter of the crystallites and the pores between them is 50 Å.

First we consider an isolated crystallite. There will be of order 1000 — 10000 atoms in a crystallite which allows the use of continuum theory to estimate the lowest eigenfrequencies. The vibrations of a homogeneous spherical body were calculated by Lamb[5] and by Tamura et al.[6] who give for the lowest eigenfrequency $\omega_{min} \approx 2.5v^{crystal}/R$. Here $v^{crystal}$ is the average transverse sound velocity in the crystalline material and R the radius of the particle. The corresponding eigenmode is mostly concentrated on the surface of the particle. Such modes have been observed e.g. by Raman scattering on nucleated glass [7].

The long-wavelength dynamics and elastic behavior of polycrystalline and similar materials is a long standing problem, e.g. [8–10]. For our purpose a simple estimate is sufficient. In aerosols one observes a scaling of the sound velocity with the density ρ : $\bar{v} \propto \bar{\rho}^{1.4}$ [11] where the bar indicates the average over the sample. We expect a similar dependence for the porous material considered here. Taking the relation $\bar{v} = \sqrt{\bar{C}/\bar{\rho}}$ we find $\bar{C} \propto \bar{\rho}^{3.8}$, where \bar{C} and $\bar{\rho}$ are the averaged elastic constant and mass density, respectively. Since the inter-atomic bonds inside the crystallites will not be affected strongly by porosity the elastic weakening reflects the weak bonding between the crystallites. The elastic constants are given by strength and number of bonds. The reduction of \bar{C} by more than a factor 10 reflects a similar reduction in the number of bonds between the crystallites.

Regarding elastic waves (with wavelengths much larger than the inter-particle distance) the porous material can be considered as an elastic medium whose properties are characterized by the average density $\bar{\rho}$ and average elastic moduli \bar{C}_{ilmn} , the averaging being over length scales much larger than the inter-particle distance. Alternatively one can look upon the problem from an equivalent point of view. In a good approximation the harmonic dynamics of elastic waves in the porous material can be described by weakly coupled rigid particles. In this amorphous lattice of crystallites the diameter $2R$ will take the role of the lattice constant inside the particles. The maximal frequency of the acoustic waves is then $\omega(q_{max}) \approx \pi\bar{v}/R$.

We consider the case $\omega_{min} > \omega(q_{max})$ and further stipulate that the relative spread, due to variations of diameter and shape, of the lowest intra particle vibration frequencies is larger than the linear coupling between these modes in adjacent crystallites. This means that the modes in the adjacent crystallites are entirely *out of resonance*. Then the eigenmodes of the crystallites are localized in the true sense of harmonic lattice theory.

Their amplitudes will decay exponentially in space into the adjoining material. This decay is the faster the larger the difference between the two frequencies. As they are true eigenmodes their time dependence is harmonic. This means that if one neglects anharmonicity *they do not decay in time at all*. If one treats the site-diagonal disorder as a perturbation one can get a lifetime as the imaginary part of the phonon self-energy. As is well known, such a lifetime would be spurious as such an imaginary part would not correspond to any attenuation. It is due only to the fact that in the presence of disorder a phonon wave vector is a poor quantum number.

Thus the lifetimes of the local vibrations are determined by anharmonicity. We consider low temperatures where in thermal equilibrium the occupation numbers of the phonons are essentially zero and transitions are dominated by phonon emission. We will show that, compared to typical crystalline samples, the anharmonic effects are so strongly reduced that the lifetimes of the low frequency localized vibrations become extremely long.

The elastic displacement within an isolated particle ℓ corresponding to the lowest eigenstate is given by [12]

$$u_i(\mathbf{r}) = \sqrt{\frac{\hbar}{2\omega_\ell \rho \mathcal{V}}} (c_\ell + c_\ell^\dagger) f_i^{(\ell)}(\mathbf{r}) \quad (1)$$

where c_ℓ and c_ℓ^\dagger are annihilation and creation operators of the lowest eigenmode in particle ℓ , ρ is the mass density of the crystallites. The eigenfunctions $f^{(\ell)}(\mathbf{r})$ satisfy the equations of elasticity theory and the normalization condition

$$\frac{1}{\mathcal{V}} \int_{\mathcal{V}} d^3r [f^{(\ell)}]^2 = 1 \quad (2)$$

with \mathcal{V} the volume of the particle. The Hamiltonian of particle ℓ is

$$H_\ell = \hbar\omega^{(\ell)} \left(c_\ell^\dagger c_\ell + 1/2 \right).$$

Consider two adjacent particles, 1 and 2, which are weakly harmonically coupled. The coupling Hamiltonian is

$$H_{12} = \eta \hbar \sqrt{\omega_1 \omega_2} \left(c_1^\dagger c_2 + c_2^\dagger c_1 \right) \quad (3)$$

where $\eta \ll 1$. The eigenfrequencies of the two particles will not differ strongly and

$$|\omega^{(1)} - \omega^{(2)}|/\omega^{(1)} \ll 1. \quad (4)$$

In places such as Eq.(3) we need not discriminate between $\omega^{(1)}$ and $\omega^{(2)}$ and we will replace them by some average value $\tilde{\omega}$. In order to make perturbation theory applicable the inter-particle coupling has to obey the inequality

$$\eta \frac{\tilde{\omega}}{|\omega^{(1)} - \omega^{(2)}|} \ll 1. \quad (5)$$

In this limit the localized vibrational states of the two particles mix only weakly. Indeed, the vibrational amplitude which is normalized to unity within particle 1 acquires an extra small factor (5) in particle 2, etc.

We take $\omega^{(1)} > \omega^{(2)}$. Then an excitation in particle 1 can decay into one in particle 2 by passing the surplus energy to a travelling acoustic wave with frequency $\omega_{\mathbf{q}} = \bar{\nu}q$

$$\omega^{(1)} = \omega^{(2)} + \omega_{\mathbf{q}}. \quad (6)$$

The energy density for the anharmonic interaction, \mathcal{E} can be written as [6]

$$\mathcal{E} = \frac{1}{6} \sum_{\substack{bc \\ itm}} C_{ialbmc}^{(3)} u_{ai} u_{bl} u_{cm}$$

where $u_{ai} = \partial u_a / \partial x_i$ and $C_{ialbmc}^{(3)}$ is the tensor of anharmonic moduli of third order which numerically are usually somewhat bigger than the harmonic moduli.

The matrix element of the process described by Eq.(6) is

$$\langle (1) | \mathcal{E} | (2), \mathbf{q} \rangle = \frac{1}{6} \sum_{\substack{bc \\ itm}} C_{ialbmc}^{(3)} \int d^3r \langle (1) | u_{ai} u_{bl} u_{cm} | (2), \mathbf{q} \rangle, \quad (7)$$

where

$$|(1)\rangle = c_1^\dagger |0\rangle, \quad |(2), \mathbf{q}\rangle = c_2^\dagger c_{\mathbf{q}}^\dagger |0\rangle$$

and $|0\rangle$ is the vacuum state with no phonons excited. To estimate the anharmonic interaction within particle 1 we write

$$\mathbf{u} = \mathbf{u}^{(1)} + \mathbf{u}^{(2)} + \mathbf{u}^{(\text{ph})},$$

where the displacement due to the travelling acoustic phonon is

$$\mathbf{u}^{(\text{ph})} = \sqrt{\frac{\hbar}{2\bar{\rho}\mathcal{V}_N}} \sum_{\mathbf{q}} \frac{1}{\sqrt{\omega_{\mathbf{q}}}} \mathbf{e}(\mathbf{q}) \exp(i\mathbf{q}\mathbf{r}) (c_{\mathbf{q}} + c_{-\mathbf{q}}^\dagger). \quad (8)$$

We imply summation over the acoustic branches with polarization vectors $\mathbf{e}(\mathbf{q})$. Unlike the particle volume \mathcal{V} in Eq.(1) \mathcal{V}_N is a normalization volume which drops out in the final result.

The local displacement of particle 1 has now, additionally to Eq.(1), a term given by Eq.(3) describing the “leak” of the vibrational state $\omega^{(2)}$ from particle 2 into particle 1

$$\mathbf{u}^{(1)} = \sqrt{\frac{\hbar}{2\omega_1 \rho \mathcal{V}_1}} \mathbf{f}^{(1)}(\mathbf{r}) \left[(c_1 + c_1^\dagger) + \eta \frac{\bar{\omega}}{\omega^{(1)} - \omega^{(2)}} (c_2 + c_2^\dagger) \right]. \quad (9)$$

For $\mathbf{u}^{(2)}$ we have the same equation replacing $1 \leftrightarrow 2$. Inserting Eqs.(9) and (8) into Eq.(7) we get after the integration

$$\langle (1) | \mathcal{E} | (2), \mathbf{q} \rangle = i(\mathcal{E}^{(1)} + \mathcal{E}^{(2)}) \langle (1) | c_1^\dagger c_2 c_{\mathbf{q}} | (2), \mathbf{q} \rangle, \quad (10)$$

where $\mathcal{E}^{(1)}$ and $\mathcal{E}^{(2)}$ are the results of integration over volumes \mathcal{V}_1 and \mathcal{V}_2 , respectively, and

$$\mathcal{E}^{(1)} = \eta \frac{\hbar}{2\rho} \sum_{\mathbf{q}} \sqrt{\frac{\hbar}{2\bar{\rho}\omega_{\mathbf{q}}\mathcal{V}}} \frac{1}{\omega^{(1)} - \omega^{(2)}} \sum_{cm} b_{mc}^{(1)} e_c q_m$$

with

$$b_{mc}^{(1)} = \sum_b \frac{1}{\mathcal{V}_1} C_{ialbmc}^{(3)} \int_{\mathcal{V}_1} d^3r \frac{\partial f_a^{(1)}}{\partial x_i} \frac{\partial f_b^{(1)}}{\partial x_l} \exp(i\mathbf{q}\mathbf{r}).$$

Again the equation for $\mathcal{E}^{(2)}$ is obtained by interchanging $1 \leftrightarrow 2$. As qL (where L is the diameter of the particle) is assumed to be small we replace the factor $\exp(i\mathbf{q}\mathbf{r})$ by 1.

Now the decay probability of the vibration in particle 1 can be calculated by Fermi's golden rule. Summing over \mathbf{q} one gets

$$\Gamma = \frac{\pi\eta^2\hbar}{4\rho^2\bar{\rho}} \left\langle \left(\sum_{cm} b_{mc} n_m e_c \right)^2 \right\rangle_{\Omega} \int_{\Omega} \frac{d^3q}{(2\pi)^3} \frac{q^2}{\omega_{\mathbf{q}}^3} \delta(\omega^{(1)} - \omega^{(2)} - \omega_{\mathbf{q}}),$$

where $\mathbf{n} = \mathbf{q}/q$ and $\langle \dots \rangle_{\Omega}$ denotes the average over the solid angle of directions \mathbf{n} .

Not knowing the exact dependence of the sound velocity \bar{v} on the average density we assume as a rough estimate, in analogy to the aerogels [11], $\bar{\rho} \propto \bar{v}$ neglecting the observed small deviations from the proportionality. Introducing the density ratio $\alpha = \bar{\rho}/\rho$ we get

$$\Gamma = \frac{\eta^2\hbar\omega_{\mathbf{q}}}{8\pi\alpha^6\rho^3v^5} \left\langle \left(\sum_{cm} b_{mc} n_m e_c \right)^2 \right\rangle_{\Omega}. \quad (11)$$

For the orientational average we apply the estimate

$$\left\langle \left(\sum_{cm} b_{mc} n_m e_c \right)^2 \right\rangle_{\Omega} \approx \zeta^2 \rho^2 v^4 \left(\frac{\pi}{L} \right)^4.$$

Here we used that the cubic anharmonic moduli are roughly of the same order as the harmonic ones. The factor ζ represents their ratio which may be equal to several units. Finally we get the following approximate value for the decay constant

$$\Gamma \approx \mathcal{N} \frac{\eta^2 \pi^3 \zeta^2 \hbar \overline{\omega_{\mathbf{q}}}}{8\alpha^6 \rho v L^4}. \quad (12)$$

Here $\overline{\omega_{\mathbf{q}}}$ is the average positive frequency difference $\omega^{(1)} - \omega^{(2)}$, \mathcal{N} is the number of neighbors to which the particle of interest is connected by chemical bonds and whose lowest eigenfrequencies $\omega^{(t)}$ are smaller than $\omega^{(1)}$ and $\overline{\eta^2}$ is the average squared coupling constant to these neighbors. \mathcal{N} can vary between 1 and a dozen.

From Eq. (12) one can get a rough estimate of the limits to be expected for the decay constant Γ . Let us assume the following values for the parameters: $\overline{\eta^2} = 10^{-3}$; $\alpha^6 = 10^{-2}$ (cf. with [1]); $\overline{\omega_{\mathbf{q}}} = 10^{11} \text{s}^{-1}$; $\rho = 5 \text{ g/cm}^3$; $v = 2 \cdot 10^5 \text{ cm/s}$; $L = 5 \cdot 10^{-7} \text{ cm}$, ζ^2 can have the typical value of several units. In particular depending on the value of \mathcal{N} we thus get Γ values of about $10^3 - 10^4 \text{ s}^{-1}$ as observed in the experiment [1].

There are some major sources of ambiguities in such an estimate. The relative inter-particle strength, $\overline{\eta^2}$, may be larger than 10^{-3} . It would be helpful to develop methods for its experimental determination. Measurements of the elastic constants and sound velocities of the porous sample would provide a more reliable estimate. The spread in the eigenfrequencies $\overline{\omega_{\mathbf{q}}}$ can, in principle, be determined by a careful optical investigation.

It is necessary to check the validity of the relation $\bar{\rho} \propto \bar{v}$. A lot could be learned from an investigation of the form of the particles constituting the sample and from their

relative spatial arrangement. (We are not giving estimates for a rather rare case where all the adjacent particles have frequencies bigger than $\omega^{(1)}$. For such particles the decay constant would be proportional to η^4 rather than to η^2 .)

Simultaneous measurements of the average mass density $\bar{\rho}$ and the average sound velocity \bar{v} should help towards an understanding of the weak attenuation of the eigenmodes in the mesoscopic crystallites. Each of these crystallites should have its own decay rate — because of different sizes and harmonic coupling constants, numbers of neighbors, etc. The observation of a non-exponential overall decay [1] is, therefore, not surprising.

In summary, we have calculated the low temperature decay rate of an ultrasonic vibration in a mesoscopic crystalline particle weakly coupled to one or several other such particles of approximately the same size. The decay time depends on the width of the distribution of particles' sizes, and the strengths of the harmonic and anharmonic couplings. Under the described limiting conditions for particles of a typical size of 50 Å the decay times may be as large as several ms.

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