

Application of Mössbauer spectroscopy to study vibrations of a granular medium excited by ultrasound

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Abstract

It is shown that analysis of Mössbauer spectra of a granulated medium, immersed into the epoxy resin without hardener, allows to study mechanical vibrations of granules. In our experiments, small particles of the potassium ferrocyanide with a 1.25 micron mean size played a role of granules. This compound was enriched by ⁵⁷Fe isotope. Particle vibrations in the vibrated resin with the frequency 12.72 MHz were induced by piezo polymer film. At rest, Mössbauer spectrum of ⁵⁷Fe in the potassium ferrocyanide consists of a single line. Ultrasonic vibration of nuclei splits the line into a comb structure with a period equal to the vibration frequency. The spectrum analysis allows to estimate the vibration amplitude of particles and decay of the ultrasound in this medium. The proposed method is unique since it allows to measure subangstrom displacements of particles vibrating with several MHz frequency.

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Properties of microscopic colloidal particles suspended in viscous liquids are of interest as an example of an overdamped system where viscous forces dominate over inertial forces, see, for example, Ref. [1]. Colloids play prominent role in biophysics as sensitive probes for studying molecular forces. Moreover, acoustic attenuation in unconsolidated granular material is of interest. For example, studying sound propagation in marine sediments is important not only from the viewpoint of applications, but has a fundamental interest since it gives information about energy dissipation in a granular medium, see, for example, Ref. [2]. Many textbooks are devoted to the description of dynamics of granular and colloidal particles, their kinetics and phase transition in these systems, see, for example, Refs. [3, 4].

Experimental tracking of the granular medium dynamics in two-dimensional geometry was realized optically [5]. In three-dimensional case the measurements were performed by nuclear magnetic resonance imaging [6, 7], x-ray technique [8], and by tracking a thin layer of radioactive particles placed between two layers of the test material [9]. Accuracy of these measurements is not high. Moreover, the listed methods allow to study only low frequency vibrations of particles. In this paper we report the results of our study of colloidal particles vibration on ultrasound frequency by gamma-radiation with 14.4 keV energy. The wavelength of this radiation field is slightly less than one Angstrom (86 pm). The proposed method allows to study vibration of colloidal particles with extremely small amplitudes. Information about attenuation of sound propagating in colloidal medium along the direction of gamma-radiation contains in the distribution of the vibration amplitudes along this direction.

This method of the vibration amplitude measurement is based on particular properties of gamma-radiation interaction with harmonically vibrated nuclei. We use solid state particles (crystals) containing nuclear isotope ^{57}Fe , which has a single absorption line of gamma-radiation at rest, i.e., when particles do not vibrate. When particles vibrate harmonically with the frequency Ω , then this line is split into a comb structure with the period Ω [10–15].

The nature of this phenomenon is explained as follows. Let a nucleus harmonically vibrates along the direction of the gamma-radiation propagation and a distance between the nucleus and the radiation source changes according to the law $R(t) = R_0 + r_0 \sin(\Omega t + \psi)$, where R_0 is that part of the distance, which is fixed, r_0 is the amplitude, Ω is the frequency, and ψ is the phase of the mechanical vibrations. Then, in the coordinate system of the moving nucleus the radiation field is transformed as $E_S[t, R(t)] =$

$E_0(t) \exp[-i\omega_S t + ikR_0 + i\varphi(t)]$, where $E_0(t)$, ω_S , and k are the amplitude, frequency and the wave number of the radiation field, respectively, $\varphi(t) = m \sin(\Omega t + \psi)$ is the periodically oscillating phase, $m = 2\pi r_0/\lambda$ is the phase modulation index, and λ is the wavelength of the radiation field. According to the Jacobi-Anger expansion the radiation field, $E_S[t, R(t)]$, can be expressed as polychromatic field consisting of a set of spectral lines $\omega_S - n\Omega$ ($n = 0, \pm 1, \pm 2, \dots$), i.e.,

$$E_S[t, R(t)] = E_C(t) e^{-i\omega_S t + ikR_0} \sum_{n=-\infty}^{+\infty} J_n(m) e^{in(\Omega t + \psi)}, \quad (1)$$

where $E_C(t)$ is the time dependent amplitude of the field, which is the same for all spectral components, and $J_n(m)$ is the Bessel function of the n -th order. The Fourier transform of this field is

$$E_S(\omega) = E_0 e^{ikR_0} \sum_{n=-\infty}^{+\infty} J_n(m) e^{in\psi} E_0(\omega_S - n\Omega - \omega), \quad (2)$$

where $E_0(\omega_S - \omega)$ is the spectrum of the source field.

Changing the frequency of the radiation source by the Doppler effect, one can observe the comb structure in the transmission spectrum of the absorber, harmonically vibrated as a whole. Absorption lines appear each time when particular frequency $\omega_S - n\Omega$ of the comb is in resonance with a single line absorber with frequency ω_A .

In Mössbauer spectroscopy the dependence of the number of photon counts on Doppler shift Δ gives the spectrum, which for simplicity can be described as

$$N_{out}(\Delta) = \sum_{n=-\infty}^{+\infty} J_n^2(m) L_n(\Delta), \quad (3)$$

where $\Delta = \omega_S - n\Omega - \omega_A$ is the difference of the resonant frequency of the single line absorber and the frequency of the spectral component $\omega_S - n\Omega$ of the source in the vibrated reference frame, $L_n(\Delta)$ is the transmission function of the single line absorber.

According to Eq. (3), the depth of the n -th component of the absorption line in the transmission spectrum is proportional to the spectral density of the n -th component of the frequency comb since only this component interacts with the absorber, and the other components propagate through without resonant interaction. Therefore, the intensity of the transmitted radiation for the n -th resonance is proportional to $1 - J_n^2(m)[1 - L_n(\Delta)]$. For the optically thick absorber we have $L_n(0) \rightarrow 0$, and the value of the dip in the transmission spectrum is proportional to $1 - J_n^2(m)$.

The Bessel function $J_n(m)$ oscillates with increase of m . For example, for $m = 2.4$ the central absorption line must disappear since $J_0(2.4) = 0$. Multidirectional evolution of the depths of the absorption lines around the modulation index value $m = 2.4$, i.e., decreasing of the central line with $n = 0$ and growing of the first side satellites with $n = \pm 1$, was observed in Refs. [13–15]. Also, zero spectral density of the central component of the radiation field ($n = 0$) at $m = 2.4$ leads to the acoustically induced transparency of the resonant absorber, which was proposed and experimentally observed in Ref. [16].

However, multidirectional dependence (decreasing/increasing) of the spectral components of the vibrated absorber with increase of the modulation index m was experimentally observed only in bulk solids, for example, in stainless-steel (SS) foil, which vibrates almost uniformly. Such a medium we name hard. Vibrations of SS foil were studied in Refs. [14, 15]. There, it was shown that SS foil vibrates as a whole (piston like). Moreover, in Ref. [15], the lead mask with a small round hole 0.6 mm in diameter was used. This mask allowed to track vibrations of small parts of the foil individually demonstrating that they vibrate almost uniformly.

Absorption spectra of powder samples dispersed in Perspex cement [11] or pressed into a tablet [14] look very different. We name such samples as elastic. Central component of their spectra has always the largest depth, while the depths of other components monotonously decrease with increasing number n . The spectra of this shape are observed for all values of the modulation index m . Moreover, the number of the observed components increases with increasing m .

These features of the experimentally observed spectra of the elastic media contradict Eq. (3). To explain experimental results the Abragam’s model [17] was applied in Refs. [11, 12, 18, 19] assuming that nuclei vibrate independently of each other with random phases ψ . The phase randomness allows to introduce the Rayleigh distribution of the vibration amplitudes of nuclei. Averaging $\langle J_n^2(m) \rangle_R$ with this distribution changes the dependence of the n -th absorption line in the spectrum, which is described then by the function $\langle J_n^2(m) \rangle_R = e^{-\langle m^2 \rangle} I_n(\langle m^2 \rangle)$, where $I_n(\langle m^2 \rangle)$ is the modified Bessel function of the n -th order and r_G is the standard deviation of the random vibration amplitude from zero value. Qualitatively, this dependence agrees with experimental spectra of the elastic media experiencing harmonic vibrations. However, quantitative fitting by this function is poor [14]. Moreover, according to the theory, developed in Ref. [20], random phase of nuclear vibrations must lead to the

appreciable decay of the harmonics in time domain spectra, which was not observed in the experiment [20]. Random phase fluctuation of the vibrating nuclei should give also extra broadening of spectral components of the comb increasing with the number n . This follows from the expression for the n -th component of the field, $e^{in\psi} E_0(\omega_S - n\Omega - \omega)$, in Eq. (2), where random phase $n\psi$ is present. Such a broadening is not observed as well.

In this paper we present the results of our new experiments with sodium ferrocyanide $K_4Fe(CN)_6 \cdot 3H_2O$. In the previous report [14] we worked with the pressed powder of this salt. In the experiments, which we report here, powder crystals of sodium ferrocyanide were grind up and stirred in epoxy resin without hardener. The granulated crystals obeyed to lognormal distribution with 1.3 μm median size and standard deviation $\sigma = 0.18$. The experimental spectra are shown in Fig 1. They are described well by the averaging of the vibration amplitude distribution proposed in Refs. [14, 15]. This distribution is

$$\langle J_n^2(m) \rangle_G = \frac{\sqrt{\frac{2}{\pi}} \int_0^\infty \exp\left[-\frac{1}{2}\left(x - \frac{1}{\varepsilon}\right)^2\right] J_n^2(\varepsilon m_c x) dx}{1 + \operatorname{erf}\left(\frac{1}{\sqrt{2}\varepsilon}\right)}, \quad (4)$$

where $m_c = 2\pi r_c/\lambda$, r_c is the mean value of the vibration amplitude and εr_c is the standard deviation, i.e., ε describes relative scattering of the amplitudes with respect to its mean value. In the model [14, 15], it is assumed that nuclei vibrate coherently but with different amplitudes, which satisfy the Gaussian distribution, $G_{\text{norm}}(r, r_c)$, centered at the value r_c with the standard deviation εr_c . Taking into account the normalization and redefying variables and parameters we obtain Eq. (4).

Spectrum analysis shows that the scattering of the amplitudes has almost the same value $\varepsilon = 0.55$ for different amplitudes of the radio frequency (RF) field. Dependence of the mean value of the modulation index on the voltage of the RF generator is shown in Fig. 2(a). Modulation index grows almost linearly with the increase of the RF field amplitude. Distribution function of the vibration amplitudes is shown in Fig. 2(b) for the RF voltage 8 V and $\varepsilon = 0.55$.

We also made experiments using the led mask with a small round hole 0.6 mm in diameter. In the previously reported experiment [15] this mask allowed to observe spectra of different small parts of the vibrated SS foil. It was found that within an area 0.6 mm in diameter the foil vibrates almost uniformly. Meanwhile, the vibration amplitudes at the foil center and at its edges strongly differ. Periodical displacements at the edges almost 1.5 times

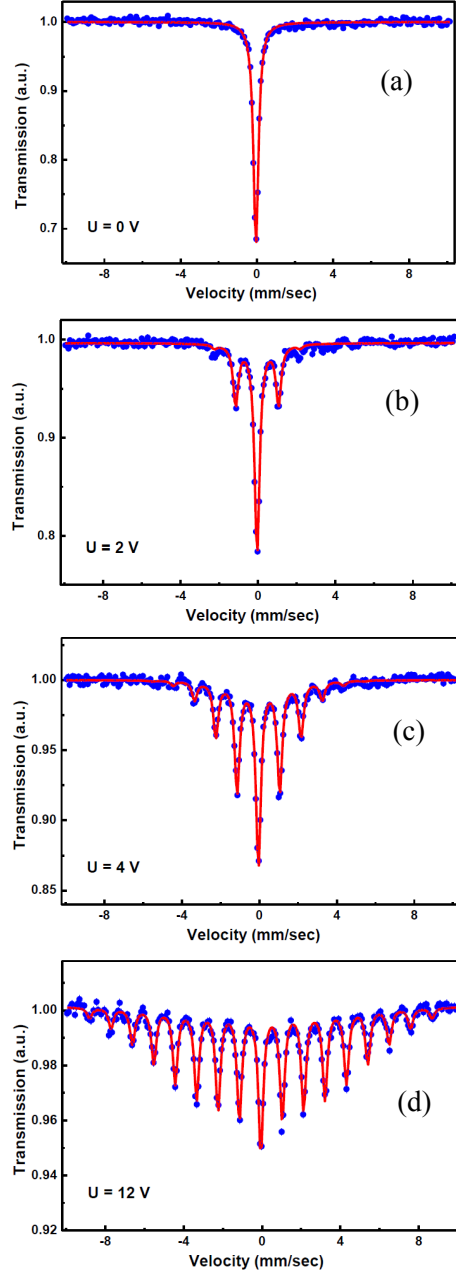


FIG. 1: Absorption spectra of the sodium ferrocyanide powder dispersed in the epoxy resin. Vertical scale is the radiation transmission normalized to unity far from any resonance. Horizontal scale is the velocity of the source in mm/sec. Piezo transducer was fed by RF voltage with 12.27 MHz frequency. The voltage is 0 V (a), 2 V (b), 4V (b), and 12 V (c). Experimental spectra are shown by blue dots and theoretical fitting by Eq. (4) is depicted by red solid line.

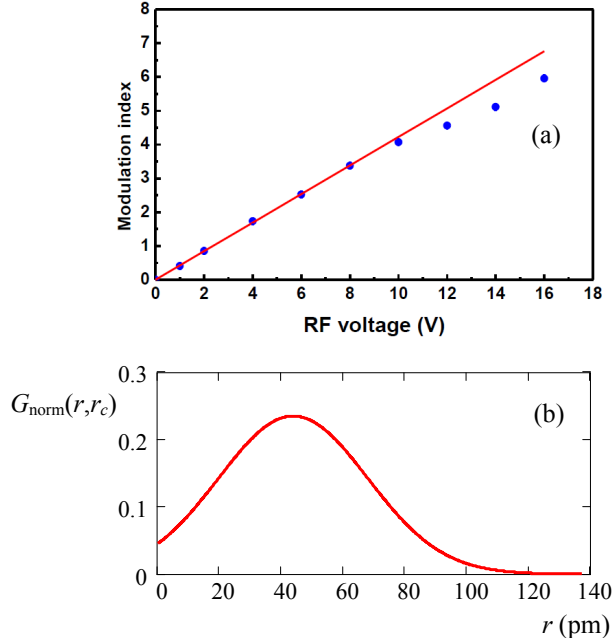


FIG. 2: (a) Dependence of the mean value of the modulation index on the voltage of the RF generator. (b) Distribution of the vibration amplitudes of iron nuclei in epoxy resin, $G_{\text{norm}}(r, r_c)$, for 8 V. Horizontal scale is in picometers.

larger than at the center. This can be explained by the small density of the polymer piezo transducer (PVDF), creating periodical displacements, with respect to the density of SS foil of approximately the same thickness as PVDF film. Therefore, the film is loaded larger at its center and smaller at the edges. This explains the difference of the foil spectra at the foil center and at its edges. Moreover, SS foil was glued to PVDF film by the polymerized epoxy glue. Since SS foil is rigid against extension, extra resistance appears to the PVDF film deformation in the longitudinal direction, i.e., to the stretching and shortening of the polymer chains, aligned along the film and producing the film surface vibration due to lengthening/shortening.

The absorber, which we use in this paper, is a spot of epoxy resin (5×5 mm) containing colloidal particles of sodium ferrocyanide. The density of this absorber is comparable with the density of the polymer piezo transducer. Moreover, epoxy resin without hardener should not create a resistance to the PVDF film movements. Therefore, we expected that the center and the edges of the absorber will vibrate with the same amplitude. Scanning of the led mask with the small hole in two orthogonal directions showed that from point to point spectra

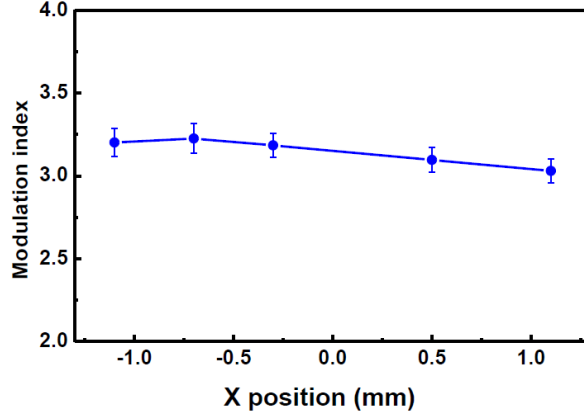


FIG. 3: Dependence of the modulation index for the same RF voltage (8 V) on the position of the hole in the mask with respect to the absorber center (in millimeters).

do not change within the accuracy of the experiment (see Fig. 3 showing the dependence of the modulation index on position of the hole along the absorber). Meanwhile, in each small area, covered by the hole, nuclei vibrate with amplitudes distributed according the function shown in Fig 2(b). This is possible if the ultrasound, induced by PVDF film, decays along the direction of gamma-radiation propagation. The particles, which are located close to the pizo transducer, i.e., at the bottom of the epoxy resin, vibrate with lager amplitude. With distance of the layer of particles from the contact of resin with PVDF the vibration amplitude decreases. This kind of distribution of the vibration amplitudes reflects a decay of ultrasound in the epoxy resin.

In conclusion we summarize our results. It is found that a single line of ^{57}Fe in colloidal particles is transformed into a central line with many satellites if the particles are vibrated by ultrasound piezo transducer. The spacing between the nearest satellites is equal to the vibration frequency. The number of the satellites depends on the vibration amplitude of nuclei and its distribution in the area of the absorber irradiated by gamma-radiation. The distribution function of the vibration amplitudes derived from comparison of experimental spectra with the theoretical predictions indicates that mechanical vibration of particles decay in the viscous medium. The obtained results demonstrate the possibility of application of gamma-resonance spectroscopy for studying the vibrational dynamics of colloidal particles immersed into a viscous medium.

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