

MÖSSBAUER ABSORPTION BY IONS IN THE HIGHLY VISCOUS LIQUIDS

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In the framework of hydrodynamic approach dynamical properties of ions are studied taking into account solvation. Density profile near the ion is described by the model potential which depends on the distance from the centre of ion. Amplitude of the potential is considered to be a fluctuating quantity. Together with random location of ions these amplitude fluctuations lead to additional disordering of a viscous liquid. For a solvated ion the linearized hydrodynamical problem is solved. For the model two-parameter potential, expressions for the dissipation function and diffusion coefficient are found. Obtained theoretical Mössbauer spectrum has the asymptotics which is typical for highly viscous liquids.

1. Introduction

Spectra of resonance gamma-quantum absorption by the dilute electrolyte solution in highly viscous liquids [1] - [4] contain a wide information about thermal motion of ion together with its environment. The simple analysis of the absorption spectra was done in the first works on Sn¹¹⁹ in polymer [2] and on Fe⁵⁷ in glycerol [3]. Despite of the success in examining the dynamical properties of electrolytes [5,6] and highly viscous liquids [7,8], the rigorous analysis of the spectra of Mössbauer absorption by ions in supercooled liquids is still absent. The Mössbauer absorption measurements on ions of ferrous chloride in glycerol [1] demonstrate nonlinear dependence of broadening on the ratio of temperature to viscosity, T/η . The dependence is close to the empiric Kohlrausch-Williams-Watts's dependence [9] - [11] which is frequently used in processing the dielectric relaxation data, NMR experiments or light scattering by supercooled amorphous liquids, polymers, other disordered systems.

In our hydrodynamic approach the dynamical properties of ions are studied taking into account solvation effect. The density profile in the vicinity of an ion in the rest is described by the effective potential $\Psi(r_i)$ of the force acting on solvent molecules [12]

$$\rho(\mathbf{r}_i) = \rho_0 \exp \left\{ -\frac{\varepsilon_i}{k_B T} \Psi(r_i) \right\}, \quad (1)$$

where ρ_0 is an average density. This effective potential is considered to be known and includes both the direct influence of the ion and indirect influence

through solvent molecules. As glycerol molecules are highly anisotropic and form into clusters at low temperatures [8], the nearest environment of localized ions is different. It can be taken into account by the random dimensionless parameter ε_i , which we take to obey the Gauss law with zero average value and dispersion $\langle \varepsilon_i^2 \rangle$.

In our approach the problem is solved in the following way. Firstly, the hydrodynamic kinetic energy and the dissipative function of a separate moving ion are found at some value of ε_i . The obtained hydrodynamic fields allow us to write the time dependent velocity correlation function of an ion. This correlation function gives the spectral density of incoherent Van Hove function [13] that describes the Mössbauer absorption spectra. Then the results are averaged over distribution of ε_i .

2. Mobility of solvatons in solvent

Due to small compressibility of real liquids the absolute value of the ratio $\Psi(r)/k_B T$ is small. It is clear from equation (1) that the force acting on unit of liquid mass near the ion equals

$$\mathbf{F} = \frac{1}{\rho} \nabla p \simeq -\frac{c^2 \varepsilon_i}{k_B T} \nabla \Psi(r_i), \quad (2)$$

where p is the pressure, c is isothermal sound velocity. Let us consider the moving ion in the coordinate system with origin at the ion. Then the problem reduces to the rest ion in the stationary flow with the velocity \mathbf{u} far from the ion. Due to the flow the density profile in the vicinity of ion changes

$$\rho(\mathbf{r}_i) = \rho_0 \exp \{-\psi(r) + \sigma(\mathbf{r})\}, \quad (3)$$

where $\psi(r) = \frac{\varepsilon_i}{k_B T} \Psi(r_i)$ and σ is the correction term describing the change of solvate shell due to the incoming flow. Using equation (2) the hydrodynamic equations of motion of liquid near the ion can be written in the form

$$\begin{aligned} \operatorname{div} \rho \mathbf{v} &= 0, \\ (\mathbf{v} \nabla) \mathbf{v} &= -c^2 \nabla \sigma + \frac{\eta}{\rho} \Delta \mathbf{v} + \frac{1}{\rho} \left(\zeta + \frac{1}{3} \eta \right) \nabla \operatorname{div} \mathbf{v}, \end{aligned} \quad (4)$$

where ζ and η are bulk and shear viscosities respectively. The fields \mathbf{v} and σ must be regular everywhere, and $\mathbf{v} \rightarrow \mathbf{u}$ at $r \rightarrow \infty$. We will search solution to (4) in the form $\mathbf{v} = \mathbf{u} + \nabla \varphi$. Then taking into account that u/c is small compared to unit one can find, after linearization of equations of motion, [12]

$$\varphi = u \cos \theta \frac{1}{r^2} \int_0^r r^2 \psi(r) dr, \quad (5)$$

$$\delta \rho = \rho - \rho_0 \simeq u \cos \theta \frac{\frac{4}{3} \eta + \zeta}{c^2} \frac{\partial \psi}{\partial r}, \quad (6)$$

where $\cos \theta = \mathbf{r} \mathbf{u} / (ru)$.

The dissipation in the fluid is determined by the expression

$$F = \int \left[2\eta (\nabla_i \nabla_k \varphi)^2 + \left(\zeta - \frac{2}{3} \eta \right) (\Delta \varphi)^2 \right] dV \quad (7)$$

and the total energy on motion of the fluid is

$$E = \frac{1}{2} \int \left[\rho_0 (\nabla \varphi)^2 + \frac{c^2}{\rho_0} (\delta \rho)^2 \right] dV, \quad (8)$$

where integration is performing over total space.

We choose the potential of an average force in the form of the two-parametric potential

$$\Psi(r) = -\varepsilon_0 \left(\frac{\tanh(r/r_0)}{r/r_0} \right)^2, \quad (9)$$

that is bounded at $r = 0$ and smoothly decreasing at $r \rightarrow \infty$. Then the dissipation function and the energy (7, 8) have the form

$$F = \frac{1}{2} u^2 6\pi r_0 \eta A^2 \tilde{\sigma}, \quad (10)$$

$$A \equiv \frac{\varepsilon_0 \varepsilon_i}{k_B T}, \quad \tilde{\sigma} \equiv \left(\frac{1}{3} + \frac{\zeta}{\eta} \right) \sigma_1 + \sigma_2,$$

$$E = \frac{1}{2} u^2 M A^2, \quad (11)$$

$$M \equiv \frac{4\pi}{3} \rho_0 (r_0 L^2 4\sigma_1 + r_0^3 \sigma_4), \quad L \equiv \frac{\eta + \frac{3}{4}\zeta}{\rho_0 c},$$

with the numerical constants

$$\begin{aligned} \sigma_1 &= \frac{4}{9} \int_0^\infty dx \left(x \frac{d \tanh^2 x}{dx} \frac{1}{x^2} \right)^2, \\ \sigma_2 &= \frac{16}{9} \int_0^\infty dx \left(\frac{\tanh^2 x}{x^2} - 3 \frac{x - \tanh x}{x^3} \right)^2, \\ \sigma_4 &= \int_0^\infty dx \left[\left(\frac{\tanh^2 x}{x^2} - 2 \frac{x - \tanh x}{x^2} \right)^2 + 2 \left(\frac{x - \tanh x}{x^2} \right)^2 \right]. \end{aligned}$$

Now it is easy to find in a usual way [14] the time dependent velocity correlation function of the solvated ion (solvaton) by means of equations (10, 11)

$$\Phi(t) \equiv \langle \mathbf{u}(t) \mathbf{u}(0) \rangle = \frac{3k_B T}{M} e^{-t/\tau_1}, \quad (12)$$

$$\frac{1}{\tau_1} \equiv \frac{6\pi r_0 \eta A^2 \tilde{\sigma}}{M} = \frac{9\tilde{\sigma}}{2\rho_0} \frac{\eta}{r_0^2 \sigma_4 + 4L^2 \sigma_1}.$$

Note that the characteristic relaxation time τ_1 in equation (12) essentially depends on viscosity directly and via L .

Let us write also the diffusion coefficient of solvation

$$D_0 = \frac{1}{3} \int_0^\infty \Phi(t) dt = \frac{k_B T}{6\pi r_0 \eta \bar{\sigma} A^2}. \quad (13)$$

3. Cross-section of resonance gamma-quantum absorption

The effective cross-section of the resonance gamma-quantum absorption is determined by the autocorrelation Van Hove function [15]

$$g(\omega) = \frac{1}{\tau_N} \int dt e^{-i\omega t - |t|/\tau_N} G_s(q, t), \quad (14)$$

where $\hbar\omega$ is the difference between energy of incident gamma-quantum and the resonance one, τ_N is the lifetime of the excited state of nucleus, $\hbar\mathbf{q}$ is the gamma-quantum impulse, and

$$G_s(q, t) = \langle \exp(-i\mathbf{q}\mathbf{r}(0)) \exp(i\mathbf{q}\mathbf{r}(t)) \rangle \quad (15)$$

is the Fourier transform of the incoherent Van Hove function. The angular brackets denote the statistical averaging. There are several model approaches to find Van Hove function. Most of them use the unfounded assumptions about time dependencies of the unknown functions and involve into consideration a lot of fitting parameters. We use the fruitful approach [10,13] based on the description of the condensed media by the projection operator method. We choose the Fourier transforms of the fluctuating local density of absorbers of gamma-quanta as the dynamical variables which are subject to averaging in equation (15)

$$\rho_q(t) = \frac{1}{N} \sum_{i=1}^N e^{i\mathbf{q}\mathbf{r}_i(t)}. \quad (16)$$

For the time dependent correlation function of fluctuations we have

$$\mathcal{I}(q, t) = \left\langle \frac{1}{N} \sum_{i=1}^N e^{i\mathbf{q} \int_0^t \mathbf{v}_i(\tau) d\tau} \right\rangle. \quad (17)$$

On the basis of the method and approximations described in [13] we find the integro-differential equation

$$\frac{d\mathcal{I}(t)}{dt} = -\frac{1}{\tau_0\tau_1} \int_0^t \tilde{\Phi}(\tau) \mathcal{I}(\tau) \mathcal{I}(t-\tau) d\tau, \quad (18)$$

where

$$\tilde{\Phi}(\tau) \equiv e^{-\tau/\tau_1}, \quad \frac{1}{\tau_0} \equiv q^2 D_0,$$

(see equations (12, 13)). Here we use the approximation that corresponds to the commensurate relaxation times of the ion velocity and coordinate, $\tau_0 \sim \tau_1$. Using the results of the viscosity measurements at different temperatures [1] one can find these relaxation times in a wide temperature range.

Equation (18) can be solved by means of Laplace transformation

$$p\mathcal{I}_p = 1 - \frac{1}{\tau_0\tau_1} \mathcal{I}_p \mathcal{I}_{p+\frac{1}{\tau_1}}. \quad (19)$$

The result can be written in the form of continued fraction

$$\mathcal{I}_p = \frac{1}{p + \frac{1}{\tau_0 \tau_1} \frac{1}{p + \frac{1}{\tau_1} + \frac{1}{\tau_0 \tau_1} \frac{1}{p + \frac{2}{\tau_1} + \frac{1}{\tau_0 \tau_1} \frac{1}{p + \frac{3}{\tau_1} + \dots}}}}. \quad (20)$$

This continued fraction is expressed via Bessel functions and the result reduces to

$$\mathcal{I}_p = \frac{1}{p + \frac{1}{\sqrt{\tau_1 \tau_0}} \frac{I_{1+p\tau_1}(2\sqrt{\tau_1/\tau_0})}{I_{p\tau_1}(2\sqrt{\tau_1/\tau_0})}}. \quad (21)$$

Note that in the limiting case of small velocity relaxation time compared to the coordinate relaxation time, $\tau_1 \ll \tau_0$, the predominant term in equation (21) is

$$\mathcal{I}_p \simeq \frac{1}{p + 1/\tau_0}, \quad (22)$$

which corresponds to the traditional approach. But after averaging over configurations of ε_i we have

$$\overline{\mathcal{I}(t)} = \exp \left\{ -\sqrt{\frac{t}{\bar{\tau}}} \right\}, \quad \frac{1}{\bar{\tau}} \equiv \frac{q^2 k_B T}{6\pi r_0 \eta \tilde{\sigma} \bar{A}^2}, \quad \bar{A}^2 = \frac{\varepsilon_0^2 \langle \varepsilon_i^2 \rangle}{(k_B T)^2}. \quad (23)$$

4. Concluding remarks

The obtained results determine the time dependance of the incoherent Van Hove function and are equivalent to the empiric Kohlrausch–Williams–Watts's low mentioned in Introduction. The analysis carried out has shown that the condition $\tau_1 \ll \tau_0$ corresponds to the supercooled state of glycerol. The general result (21) describes the Mössbauer absorption spectrum (14) and after averaging over configurations of ε_i it can be expressed as follows

$$\overline{g(\omega)} = \text{Re} \overline{\mathcal{I}_{i\omega + \frac{1}{\tau_N}}}. \quad (24)$$

The comparison of the presented dependencies with the experimental data [1] on the gamma-quantum absorption by the ions of Fe in glycerol demonstrates a good agreement the experimental temperature behaviour of the spectrum parameters with one found theoretically.

Note that the method of the random potential of solvation is the hydrodynamical analog of the description of the various disordered systems such as, for instance, glasses.

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МЕСБАУЕРІВСЬКА АБСОРБЦІЯ ІОНАМИ В СИЛЬНО В'ЯЗКИХ РІДИНАХ

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У рамках гідродинамічного підходу досліджуються динамічні властивості іонів з врахуванням сольватації. Профіль густини поблизу іону описується модельним потенціалом, що залежить від відстані від центру іону. Амплітуда потенціалу розглядається як флуктуаційна величина. Разом з випадковим розташуванням іонів ці флуктуації амплітуди приводять до додаткового безладу в'язких рідин. Розв'язується лінеаризована гідродинамічна проблема для сольватованого іона. Знаходяться вирази для дисипативної функції та коефіцієнта дифузії для модельних двопараметричних потенціалів. Отриманий теоретично месбауерівський спектр має асимптотику, що є характерною для сильно в'язких рідин.