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Influence of the concentration value of sensitizing dyes on the photovoltaic effect in monocrystalline n-type silicon in the optical region

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Abstract. This paper investigates the impact of sensitizing organic dyes located on the surface of monocrystalline n-type silicon on the character of the photovoltaic effect. It studies the sensitized photovoltaic effect with erythrosine and methylene blue dyes used as sensitizers at different concentrations. The findings are discussed from the point of view of the mechanism of nonradiative inductive-resonant transfer of energy absorbed by the sensitizing dye to the surface of silicon crystal.

Keywords: monocrystalline n-type silicon, erythrosine and methylene blue dyes, sensitized photovoltaic effect, concentration of sensitizing dyes, absorption spectra of the sensitizing dyes

Introduction

The relatively low extinction coefficient of silicon in the region of indirect transitions predetermines a serious limitation of solar cells based on this type of semiconductors; therefore, converters of light energy into electrical energy manufactured on its basis must have a comparatively large thickness (Alferov et al. 2004). In turn, spectral sensitization by dyes with an absorption band in the visible and near infrared region of the spectrum of organic dyes provides effective control over the spectrum and level of photosensitivity of classical silver halide photographic materials (James 1977). Moreover, this sensitization is widely used to increase the efficiency of photophysical and photochemical processes in various wide-band gap semiconductors (Akimov et al. 1980; Goryaev, Pimenov 1975; 1980). Photoelectrochemical cells based on titanium dioxide particles with sensitizing dyes are proposed as an alternative to silicon solar cells (Gratzel 2003). The efficiency of organic dye application is primarily determined by the high extinction coefficient in the absorption band. Spectral sensitization by dyes was observed for DC photoconductivity in powdered silicon (Goryaev 2015) and for photo-EMF in a monocrystalline semiconductor (Goryaev 2019). The paper (Goryaev, Smirnov 2025) shows that sensitization of photo-EMF is observed only in silicon with electron conductivity, and in samples with hole conductivity desensitization of the photoelectric effect occurs. Effective sensitization of photoconductivity at direct current is manifested in samples with any type of conductivity for powdered silicon (Goryaev, Smirnov 2025). This paper delves into the photovoltaic effect in n-type silicon samples and the influence of organic dyes

with absorption bands in the region of indirect electron transitions in silicon on its spectra, which are located on the surface of the semiconductor.

Experiment

This work focused on monocrystalline n-type silicon samples doped with phosphorus. The sample area was approximately 1 cm^2 , with the thickness of $360\text{--}450 \text{ }\mu\text{m}$. The photo-EMF spectra were measured using a capacitor method (Akimov 1966; Goryaev, Smirnov 2025). Adsorption of dye molecules on the surface of the samples was carried out by dosed application of an ethanol solution of a certain concentration of this dye to the sample under study. After the adsorption, the sample was dried for 1–2 days. Erythrosine and methylene blue were used as organic dyes. The samples were irradiated with modulated light, and the absorption spectra of ethanol solutions of the dyes measured using an SF-26 spectrophotometer. To adequately assess the degree of expression of the internal photoelectric effect in different regions of the spectrum, the photo-EMF signals ΔU_{ph} were normalized to the number of light quanta E incident on the sample at a corresponding wavelength.

Results and discussion

Fig. 1 shows the spectrum of the photovoltaic effect in silicon without a dye. The magnitude of photo-EMF decreases monotonically with an increasing wavelength. This behavior of spectral dependence is associated with the fact that the considered range corresponds to the region of indirect transitions in silicon. These transitions occur in a semiconductor at an energy of absorbed light quanta from 2.5 eV (the vertical gap between the valence and conduction bands of silicon) to 1.08 eV (the thermal gap between the bands at 300 K) and are characterized by a monotonic decline in absorption with decreasing energy in the specified range (Bonch-Bruevich, Kalashnikov 1977; Wert, Thomson 1969).

Erythrosine and methylene blue dyes are effective sensitizers in the visible and near infrared spectral regions (Akimov et al. 1980; Goryaev 2015). Fig. 2 shows the absorption spectra of these dyes in an ethanol solution.

The efficiency of spectral sensitization of the photovoltaic effect in a semiconductor by a dye is characterized by the value $(\Delta U/\Delta U_0)-1$, where ΔU and ΔU_0 are the measured photo-EMF signals of the dyed and undyed samples, respectively. This value shows the proportion of the sensitized photoelectric effect value to the intrinsic photoelectric effect value, and its dependence on the wavelength represents the differential spectrum of the sensitized photoelectric effect.

Fig. 3 shows the differential spectra of the sensitized photoelectric effect of silicon dyed with erythrosine (a) and methylene blue (b).

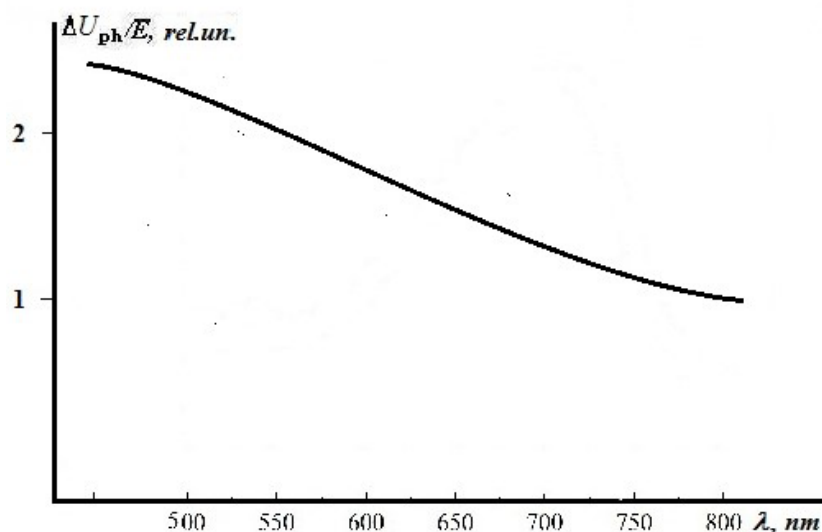


Fig. 1. Photo-EMF spectrum of silicon without a dye

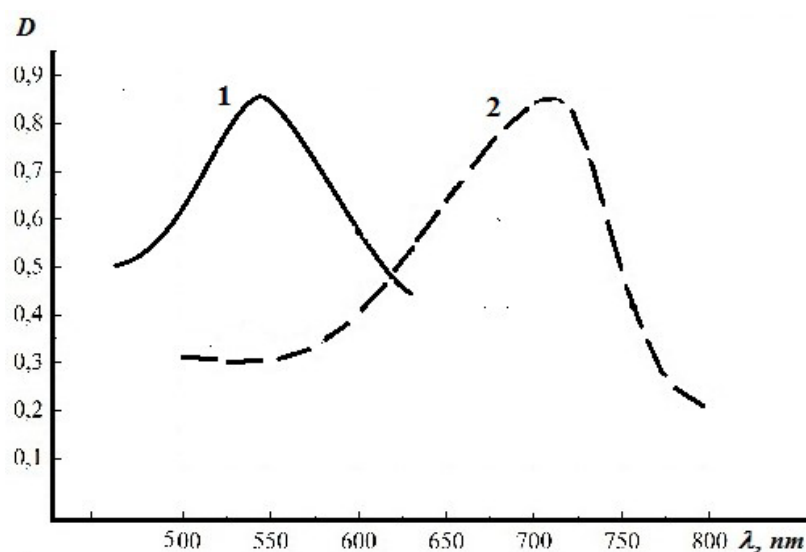


Fig. 2. Absorption spectra of erythrosine (1) and methylene blue (2) in ethanol with a dye concentration of $2 \cdot 10^{-4}$ M/L

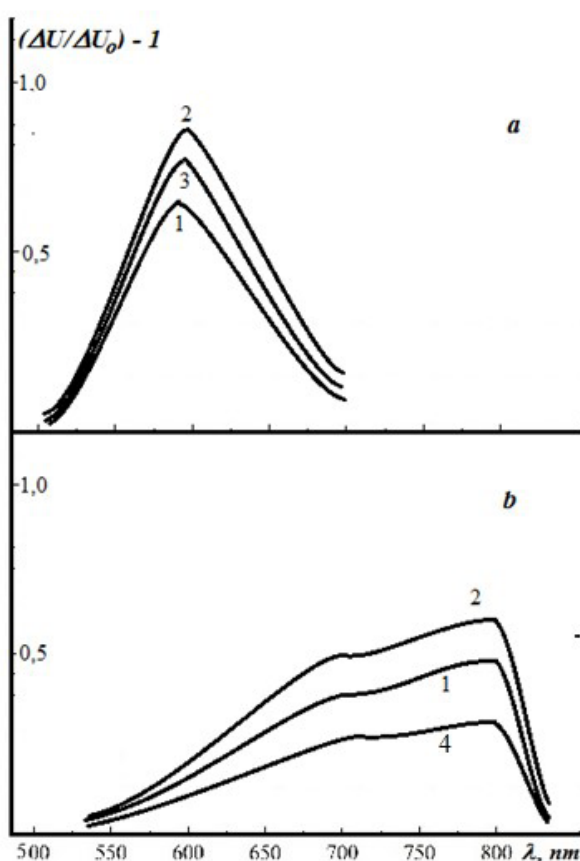


Fig. 3. Differential spectra of the sensitized photoelectric effect in dyed silicon samples with dye molecule concentrations of 40 nm^{-2} (1), 70 nm^{-2} (2), 110 nm^{-2} (3), and 210 nm^{-2} (4). a — semiconductor with an adsorbed erythrosine dye; b — semiconductor with an adsorbed methylene blue dye

When the dye concentration increases, the magnitude of the sensitized photoelectric effect rises to certain limits, reaching 80% for erythrosine and 60% for methylene blue relative to photo-EMF in an undyed sample (Fig. 3, curves 1 and 2). It should be noted that the efficiency of sensitization in the infrared region can be augmented using supersensitizers, as done in silver halide photography (Goryaev,

Shapiro 1997). A comparison between the sensitization spectra of the photoelectric effect and the absorption spectra of the dyes shows that the sensitization maxima are shifted to the longer wavelength region relative to the maxima of the absorption bands (Figs. 2 and 3). This is probably due to the interaction of the dyes with the semiconductor surface during adsorption (Akimov et al. 1980; Goryaev, Pimenov 1980). Also playing a role in this shift is the fact that the first phase of the sensitization process is the nonradiative transfer of energy absorbed by the dye to the semiconductor. According to theory, the efficiency of inductive-resonant non-radiative energy transfer depends on the overlap integral of the luminescence spectrum of the donor and the absorption spectrum of the energy acceptor (Ermolaev et al. 1996):

$$K = C \int I_d n(\nu) \varepsilon_a(\nu) \nu^{-4} d\nu,$$

where I_d is the spectral density of the donor luminescence radiation, $\varepsilon_a(\nu)$ is the molar absorption coefficient of the energy acceptor, n is the refractive index of the medium, ν is the wave number, and C is a constant. The overlap integral strongly depends on the wave number, as confirmed by a more intensive quenching of the luminescence of dyes in the long-wavelength region of the spectrum when energy is transferred to a solid (Goryaev, Akimov 1979). Therefore, the spectra of the sensitized photoelectric effect are shifted relative to the absorption spectra of the dye to the long-wave region.

The maximum efficiency of sensitization is observed at a dye concentration of 70 nm^{-2} on the semiconductor surface. If the concentration continues to rise, the photo-EMF value decreases (Fig. 3, curves 3 and 4). This is due to the fact that an increase in the dye layer thickness amplifies the role of intramolecular processes of non-radiative disappearance of absorbed energy. Furthermore, a great part of the light energy does not hit the silicon crystal, and a filter effect exists in the dye absorption band (Goryaev 1980; 2015; 2019). In turn, a low concentration of the dye on the surface of silicon crystal leads to an insufficient influence of this dye on the photovoltaic effect.

Conclusion

Organic dyes on the surface of silicon monocrystals with electronic conductivity have a sensitizing action on the photovoltaic effect in the absorption band of the dye in the region of indirect electronic transitions of the semiconductor. The optimal concentrations of the dyes have been determined for the case when the sensitized photo-EMF almost reaches the value of its own photoelectric effect. A higher amount of dye applied to the semiconductor is associated with a filter effect and a significant reduction in the photovoltaic effect.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

Authors' contributions to the paper are equal.

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Analytical solutions of two-phase region equations in the presence of an incoming flow

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Abstract. This paper describes theory behind the process of directional crystallization with a two-phase region, taking into account the presence of a two-phase region (a layer of mixed solid and liquid phases), as well as a weak outgoing or incoming flow. The analytical solution to high non-linear heat and mass transfer model is found analytically in a parametric form. The impurity concentration profile, temperature distribution, the solid phase portion, the solidification velocity, and the thickness of the two-phase region are determined analytically. The dependencies of impurity concentration versus the solid phase portion are plotted and compared with experimental data. In addition, the permeability of the two-phase region is plotted versus the spatial coordinate, and the interdendritic distance is plotted versus the crystallization rate and compared with the experimental data. In all cases, the theory discussed in this paper is in agreement with the experimental data.

Keywords: directional solidification, two-phase region, weak flow, heat and mass transfer, precise analytical solutions, nonlinear systems of equations

Introduction

A controlled and regulated crystallization process allows the creation of materials with a given structure, desired characteristics, and properties (Alexandrov et al. 2024; Batchelor 1974; Buyevich, Natalukha 1994; Ivanov et al. 2021; Kelton, Greer 2010; Makoveeva 2023; 2024; Makoveeva, Ivanov 2024; Slezov 2009; Vollmer, Raisch 2001). It is well known that the crystallization process can be directional or volumetric. Directional crystallization is caused by a temperature or concentration gradient that determines the direction of crystallization in space. Volumetric crystallization involves the nucleation and growth of crystals within a supercooled bulk of liquid. In the case of directional solidification, a curvilinear interphase boundary between solid and liquid phases moves in a certain spatial direction. Sometimes, such a boundary is not the solid-liquid interface of indefinitely small thickness, and it represents a zone of finite thickness filled with mixed solid and liquid phases. This zone is called the two-phase region.

Note that the heat and mass transfer processes in the two-phase region are influenced by various factors, and the portion of the solid and liquid phase plays a significant role. This portion affects the density, heat capacity, thermal conductivity, and diffusion coefficient of a given material (Buyevich et al. 2000; Worster 1986). Since heat and mass transfer are determined by the phases, among other things, transport equations should be written for each of the regions to describe the crystallization process.

As a result, transport equations are formulated for a purely solid phase, a two-phase region, and a purely liquid phase. To ensure the closure of the mathematical model, one should consider the boundary conditions at both boundaries of the two-phase region with a purely solid phase and a purely liquid phase. The initial and boundary conditions far from these boundaries should also be considered. Thus, we obtain a problem with heat and mass transport equations in each zone supplemented with boundary and initial conditions. This problem of heat and mass transfer is non-linear, with two moving phase transition boundaries (Aseev, Alexandrov 2006b; Buevich et al. 2000; Fowler 1985; Makoveeva et al. 2023). Such problems cannot be solved by standard methods, each problem requiring an original approach (see, for example, some previous studies (Alexandrov 2018; 2001a; Alexandrov, Alexandrova 2019; Mansurov 1990; Toropova et al. 2022)). A model of quasi-steady solidification with a two-phase region, without convection, was solved analytically by Alexandrov et al. (Alexandrov 2001b; Aseev, Alexandrov 2006a) using the transition to a new variable — the solid-phase portion. Subsequently, the nucleation and growth of particles in a two-phase region were taken into account, and this problem was solved analytically in Refs. (Alexandrov, Malygin 2006; Toropova et al. 2022). Worster was the first to consider a self-similar process, analyzing it numerically (Buevich et al. 2000). Subsequently, this process was analytically studied using a series expansion of the impurity concentration, temperature, and fraction of the solid phase in Refs. (Alexandrov et al. 2007). The LeadEx experiment on the freezing of sea ice is described using a model of non-steady-state directional solidification, which is caused by variations in the atmospheric temperature as a function of time. This problem was approximately solved in Refs. (Alexandrov, Nizovtseva 2008b; Alexandrov et al. 2008). Later, AIDJEX and SHEBA experiments on freezing sea ice from below with a false bottom formed were also described in Refs. (Alexandrov, Malygin 2011; Alexandrov, Nizovtseva 2008a; Worster 1991).

This paper examines the directional crystallization process with a two-phase region. Weak convection, i. e., a flow directed away from or toward the two-phase region, is also included in the model. The two-phase region solidifies at a constant rate. In addition, the present analysis is based on the methods of Refs. (Alexandrov 2001b; Aseev, Alexandrov 2006a).

Directed steady-state crystallization with a two-phase region

We consider a directed crystallization process along the spatial axis ζ . The crystallization rate v is constant. The process is determined by given temperature gradients in the solid and liquid phases, g_s and g_l , respectively (the process model is shown in Fig. 1). We introduce the following notations: τ is time, and δ is the thickness of the two-phase region. Shown at the top in Fig. 1 is the region with a purely solid phase, at $\zeta < v\tau$. Next, from top to bottom, is the two-phase region for $v\tau < \zeta < v\tau + \delta$. In the last region, there is a purely liquid phase, $\zeta > v\tau + \delta$.

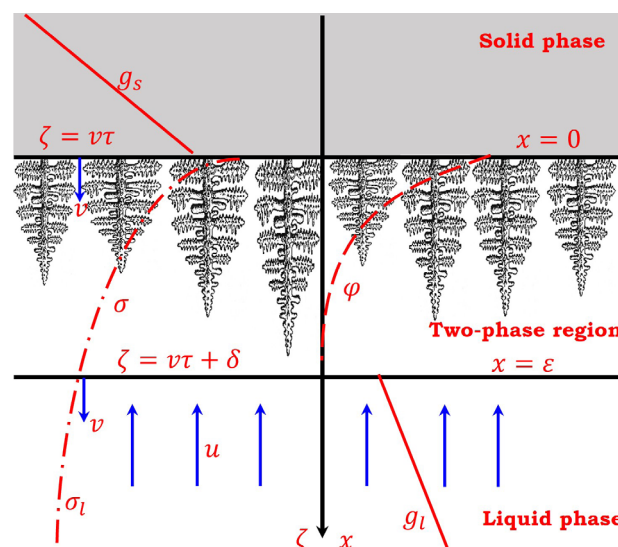


Fig. 1. A scheme of steady-state directed crystallization with constant velocity v along the ζ -axis. The solid phase — two-phase region and two-phase region — liquid phase boundaries are respectively located at $\zeta = v\tau$ ($x = 0$) and $\zeta = v\tau + \delta$ ($x = \varepsilon$). The solid, dash-dotted, and dashed lines schematically illustrate the temperature, impurity concentration, and solid phase portion distributions, respectively

The two-phase zone is a mixed zone consisting of both phases. The solid phase consists of dendritic structures, between which there is a liquid phase, represented by a molten melt. We also take into account that weak convection may occur in the liquid phase, the influence of which leads to a change in the distribution of impurities in the two-phase region and in the interdendritic space. This change in impurity distribution influences how the solid-phase impurity is absorbed by the solidifying liquid phase.

To present the process described above, heat and mass transfer equations will be required in the following form (Alexandrov et al. 2023; Kaviani, Kanury 2002):

$$\rho(\varphi)c(\varphi)\frac{\partial\vartheta}{\partial\tau} + \rho_l c_l(1-\varphi)\mathbf{u} \cdot \nabla\vartheta = \nabla(\lambda(\varphi)\nabla\vartheta) + L_v \frac{\partial\varphi}{\partial\tau}, v\tau < \zeta < v\tau + \delta, \quad (1)$$

$$\frac{\partial}{\partial\tau}((1-\varphi)\sigma) + (1-\varphi)\mathbf{u} \cdot \nabla\sigma = \nabla(D(\varphi)\nabla\sigma) - k\sigma \frac{\partial\varphi}{\partial\tau} - 2\alpha k\varphi \frac{\partial\sigma}{\partial\tau}, \quad (2)$$

$$v\tau < \zeta < v\tau + \delta,$$

where ϑ , σ , and φ are the temperature, impurity concentration, and portion of the solid phase in the two-phase region, $\mathbf{u}$ is the velocity of the liquid, L_v is the latent heat parameter, k is the distribution coefficient determining the portion of impurity absorbed by the solid phase, and α is the back diffusion in the solid state (for more details, see Appendix 12 in (Mullins, Sekerka 1964)). The functions φ can be written as a superposition of the transport coefficients in the solid and liquid phases (Buevich et al. 2000; Worster 1986). The functions of φ are: density ρ , heat capacity c , thermal conductivity λ , and diffusion coefficient D of the impurity

$$\begin{aligned} \rho(\varphi)c(\varphi) &= \rho_s c_s \varphi + \rho_l c_l(1-\varphi), \\ \lambda(\varphi) &= \lambda_s \varphi + \lambda_l(1-\varphi), \end{aligned} \quad (3)$$

$$D(\varphi) = D_l(1-\varphi),$$

where the indices s and l denote the properties of solid and liquid, respectively. The theory outlined in this paper takes into account that the heat and mass transfer coefficients are arbitrary functions of φ .

Note that the characteristic values of the relaxation times of the temperature (τ_ϑ) and concentration (τ_σ) fields are known. As a result, we can simplify models (1) and (2) by introducing a characteristic length scale: $\tau_\vartheta = l^2/\kappa_l$ and $\tau_\sigma = l^2/D_l$, where $\kappa_l = \lambda_l/(\rho_l c_l)$ is the thermal diffusivity. We know the characteristic values of τ_ϑ and τ_σ ; that is, their ratio is also known: $\tau_\vartheta/\tau_\sigma \sim 10^{-3} - 10^{-4}$, so the left-hand side of equation (1) is significantly smaller than the right-hand side.

The crystallization process is directed along the ζ axis, while the impurity concentration gradient is directed in the opposite direction due to the displacement of impurities by the growing solid phase. Since we consider flows predominantly in one direction of the ζ axis, we can neglect heat transfer in perpendicular directions. Thus, equations (1) and (2), taking all estimates into account, will look as follows:

$$\frac{\partial}{\partial\zeta}\left(\lambda(\varphi)\frac{\partial\vartheta}{\partial\zeta}\right) + L_v \frac{\partial\varphi}{\partial\tau} = 0, v\tau < \zeta < v\tau + \delta, \quad (4)$$

$$\begin{aligned} \frac{\partial}{\partial\tau}((1-\varphi)\sigma) + (1-\varphi)u \frac{\partial\sigma}{\partial\zeta} &= \frac{\partial}{\partial\zeta}\left(D(\varphi)\frac{\partial\sigma}{\partial\zeta}\right) - \\ &- k\sigma \frac{\partial\varphi}{\partial\tau} - 2\alpha k\varphi \frac{\partial\sigma}{\partial\tau}, v\tau < \zeta < v\tau + \delta, \end{aligned} \quad (5)$$

where the positive value of the fluid velocity ($u > 0$) is chosen against the ζ axis, as shown in Fig. 1.

Let us take into account the relationship between temperature ϑ and impurity concentration σ using the liquidus equation of the form:

$$\vartheta = \vartheta_0 - m\sigma, v\tau < \zeta < v\tau + \delta, \quad (6)$$

where ϑ_0 is the phase transition temperature for the pure melt ($\sigma = 0$), and m is the slope of the liquidus line.

Taking into account that $\tau_g/\tau_\sigma \ll 1$, we obtain the following equations of heat and mass transfer in the liquid and solid phases, respectively:

$$\frac{\partial^2 \vartheta_l}{\partial \zeta^2} = 0, \frac{\partial \sigma_l}{\partial \tau} + u \frac{\partial \sigma_l}{\partial \zeta} = D_l \frac{\partial^2 \sigma_l}{\partial \zeta^2}, \zeta > v\tau + \delta, \quad (7)$$

$$\frac{\partial^2 \vartheta_s}{\partial \zeta^2} = 0, \zeta < v\tau, \quad (8)$$

where ϑ_l is the temperature of the liquid phase, ϑ_s is the temperature of the solid phase, and σ_l is the concentration of impurities. Equations (7) and (8) mean that the first derivatives of the temperatures in the liquid and solid phases define the temperature gradients $\partial \vartheta_l / \partial \zeta = g_l$ and $\partial \vartheta_s / \partial \zeta = g_s$; i. e., the temperature gradients are fixed.

Let us supplement equations (4)–(8) with boundary conditions at both boundaries of the two-phase region:

$$\varphi = \varphi_*, \lambda_s g_s - \lambda(\varphi_*) \frac{\partial \vartheta}{\partial \zeta} = L_V(1 - \varphi_*)v, \zeta = v\tau, \quad (9)$$

$$(1 - k)(1 - \varphi_*)\sigma v + D(\varphi_*) \frac{\partial \sigma}{\partial \zeta} = 0, \zeta = v\tau, \quad (10)$$

$$\varphi = 0, \lambda(0) \frac{\partial \vartheta}{\partial \zeta} = \lambda_l \frac{\partial \vartheta_l}{\partial \zeta} = \lambda_l g_l, D(0) \frac{\partial \sigma}{\partial \zeta} = D_l \frac{\partial \sigma_l}{\partial \zeta}, \zeta = v\tau + \delta, \quad (11)$$

where φ_* is the portion of the solid phase at the boundary between the solid phase and the two-phase region.

Let us set the concentration of impurities in the liquid far from the boundary $\zeta = v\tau + \delta$, that is,

$$\sigma_l \rightarrow \sigma_{l\infty}, \zeta \rightarrow \infty. \quad (12)$$

As a result, we obtained a nonlinear model (4)–(12) describing the stationary directed crystallization process with a two-phase region. The resulting model will be solved analytically in the next section.

Analytical solutions

We will analyze the mathematical model from the viewpoint of a moving reference frame. We will introduce dimensionless variables and parameters for the transition to a moving coordinate system:

$$\begin{aligned} x &= \frac{v}{D_l}(\zeta - v\tau), C = \frac{\sigma}{\sigma_{l\infty}}, C_l = \frac{\sigma_l}{\sigma_{l\infty}}, \varepsilon = \frac{v\delta}{D_l}, \\ G_l &= \frac{D_l g_l}{vm\sigma_{l\infty}}, \Lambda_1 = \frac{\lambda_l}{\lambda_s}, \Lambda_0(\varphi) = \frac{\lambda(\varphi)}{\lambda_s}, \\ P &= \frac{\lambda_s m \sigma_{l\infty}}{L_V D_l}, D_0(\varphi) = \frac{D(\varphi)}{D_l}, M(\varphi) = \frac{D_0(\varphi)}{\Lambda_0(\varphi)}. \end{aligned} \quad (13)$$

Let us first consider equation (6) — the liquidus equation. Using it, we can eliminate the temperature field from the heat transfer equations. As a result, in the new moving reference frame, equations (4) and (5) take the following form:

$$\frac{d}{dx} \left(\Lambda_0(\varphi) \frac{dC}{dx} \right) + \frac{1}{P} \frac{d\varphi}{dx} = 0, 0 < x < \varepsilon, \quad (14)$$

$$\begin{aligned}
& -\frac{d}{dx}((1-\varphi)C) + ((1-\varphi)\omega - 2\alpha k\varphi)\frac{dC}{dx} = \\
& = \frac{d}{dx}\left(D_0(\varphi)\frac{dC}{dx}\right) + kC\frac{d\varphi}{dx}, 0 < x < \varepsilon,
\end{aligned} \tag{15}$$

where $\omega = u/v$.

We obtain the impurity concentration in the two-phase region by integrating equation (14) and also taking into account the boundary conditions (11). Then the concentration derivative becomes

$$\frac{dC}{dx} = -\frac{\varphi + PG_l\Lambda_1}{P\Lambda_0(\varphi)}, 0 < x < \varepsilon. \tag{16}$$

We next combine equations (6), (9), and (16) to find the steady-state crystallization rate v

$$v = \frac{\lambda_s g_s - \lambda_l g_l}{L_v}. \tag{17}$$

An important note is that the velocity (17) during directed crystallization with a two-phase zone coincides with the velocity of a flat crystallization front (Alexandrov 2001b; Alexandrov, Galenko 2024; Brody 1965).

Let us now derive a differential equation for $C(\varphi)$. To do this, we substitute the concentration (16) into equation (15) and multiply the resulting expression by $dx/d\varphi$. This gives us the following equation for $C(\varphi)$:

$$(1-k)C + [(1-\varphi)(\omega-1) - 2\alpha k\varphi]\frac{dC}{d\varphi} + \gamma(\varphi) = 0, \tag{18}$$

where

$$\gamma(\varphi) = \frac{1}{P}\left(M(\varphi) + (\varphi + PG_l\Lambda_1)\frac{dM}{d\varphi}\right).$$

Equation (18) demonstrates that the concentration of impurities and the temperature are functions that depend only on the solid phase portion.

We now obtain concentration distribution in the liquid. We integrate equation (7) for the liquid phase and also take into account the boundary conditions (11) and (12). Then the concentration in the liquid is as follows:

$$C_l(x) = 1 + \frac{G_l}{1-\omega} \exp[-(1-\omega)(x-\varepsilon)], x > \varepsilon. \tag{19}$$

Let us find the final expression for the concentration in the two-phase zone. We integrate equation (18) taking into account the boundary condition $C_0 = C_l(\varepsilon)$, obtaining the concentration distribution in the two-phase zone:

$$\begin{aligned}
C(\varphi) = & \left[\left(1 + \frac{G_l}{1-\omega}\right) (1-\omega)^{1-s} + \int_0^\varphi \frac{\gamma(\phi)d\phi}{[(1-\omega)(1-\phi) + 2\alpha k\phi]^s} \right] \cdot \\
& \cdot [(1-\omega)(1-\varphi) + 2\alpha k\varphi]^{s-1}, 0 < x < \varepsilon,
\end{aligned} \tag{20}$$

where

$$s = \frac{(1-2\alpha)k - \omega}{1-2\alpha k - \omega}.$$

We now consider the resulting equation (20). This equation shows that the concentration of impurities is only a function of the solid phase portion. Equation (20) includes previously found solutions and generalizes them so that we can obtain limit transitions to previously found theories. To move

to the Brody–Flemings distribution (Scheil 1942), we remove the diffusion and liquid flows and let them tend to zero ($D_l \rightarrow 0$ and $\omega \rightarrow 0$). We can also obtain the classical Scheil formula (Alexandrov, Malygin 2006; Galenko 2023) with $\alpha \rightarrow 0$. Galenko obtained the distribution of the impurity concentration with weak convection and reverse diffusion (Dehnavi et al. 2015). To move on to this solution, we let the diffusion in the liquid phase tend to zero, i. e., $D_l \rightarrow 0$.

Thus, equation (20) is a solution that unifies many previous theories. The resulting dependence takes into account impurity diffusion, weak convection in the liquid, and the movement of the solidifying region during directed crystallization. It is important to note that in equation (20), the concentration of impurities completely determines the temperature in the two-phase region, in accordance with equation (6).

By differentiating $C(\varphi)$ with respect to x , we obtain $dC/dx = (dC/d\varphi)/(d\varphi/dx)$. Thus, we arrive at the distribution of the solid phase portion in the two-phase region as an inverse function of $x(\varphi)$

$$x(\varphi) = \varepsilon - P \int_0^\varphi \frac{(dC/d\phi)\Lambda_0(\phi)d\phi}{\phi + PG_l\Lambda_1}, 0 < x < \varepsilon, \quad (21)$$

where $dC/d\varphi$ is determined by expression (20).

The dimensionless thickness of the two-phase region follows from expression (21) taking into account $\varphi = \varphi_*$ at $x = 0$ and has the form:

$$\varepsilon = P \int_0^{\varphi_*} \frac{(dC/d\phi)\Lambda_0(\phi)d\phi}{\phi + PG_l\Lambda_1} \quad (22)$$

Taking this into account, we determine from (10) the solid phase portion φ_* at the interface between the solid phase and the two-phase region:

$$M(\varphi_*)(\varphi_* + PG_l\Lambda_1) = P(1 - k)(1 - \varphi_*)C(\varphi_*), \quad (23)$$

where $C(\varphi_*)$ is defined by formula (20), and φ_* is the root of the transcendental equation (23).

Thus, expressions (17), (19)–(23) represent a complete analytical solution of the stationary model of directed crystallization with weak convection.

Fig. 2 shows the solid phase concentration $C_s = kC$, where C is defined by expression (20). The Brody–Flemings model (Scheil 1942) characterizes the absence of a liquid phase, $\omega = 0$, and is indicated by a transparent solid surface. The figure also shows two possible solutions: incoming and outgoing flows. For the incoming flow, the blue line, $\omega > 0$, indicates that the concentration of impurities exceeds the concentration in the absence of a weak flow. This occurs because copper also enters the two-phase region with the flow; it affects the growth of dendrites within the two-phase region.

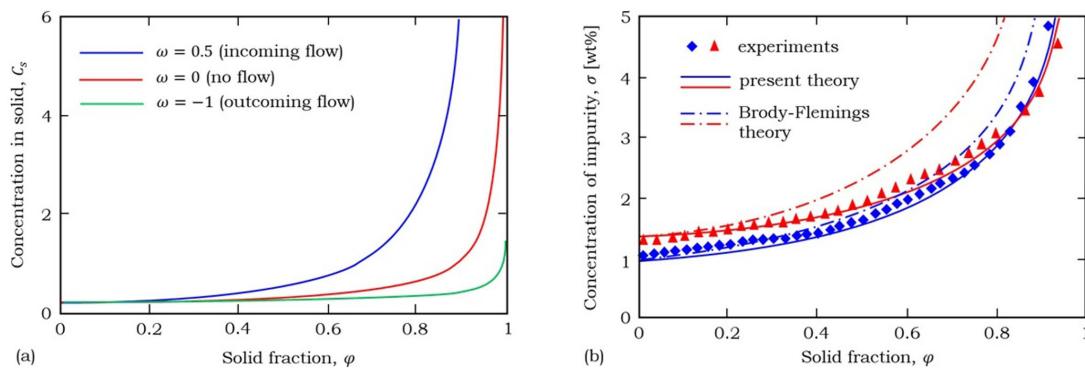


Fig. 2. (a) Dimensionless concentration in solid $C_s = kC$ for various convective flows: $\omega = 0.5$ (the incoming flow is shown in Fig. 1), $\omega = 0$ (stagnant melt), and $\omega = -1$ (outcoming flow); $\sigma_{\infty} = 5\text{wt\%}$. (b) Dimensional concentration of impurities for various convective flows: $\omega = -0.2$ ($\sigma_{\infty} = 1\text{wt\%}$, blue line) and $\omega = -0.55$ ($\sigma_{\infty} = 1.3\text{wt\%}$, red line) is compared with the experimental data (Dehnavi et al. 2015) (symbols). Dashed lines illustrate the Brody–Flemings theory (Brody 1965.) with $\omega = 0$. The physical parameters of the Al–Cu melt are presented in Table 1 with $g_s = 5 \cdot 10^2 \text{ }^\circ\text{C m}^{-1}$, $g_l = 10^2 \text{ }^\circ\text{C m}^{-1}$

Table 1. Physical parameters

Parameters	Al–Cu	Sn–Pb
λ_s [kg m s ⁻³ °C ⁻¹]	211.18	65
λ_l [kg m s ⁻³ °C ⁻¹]	90.92	33
D_l [m ² s ⁻¹]	$5 \cdot 10^{-9}$	$4.5 \cdot 10^{-9}$
L_v [kg s ⁻² m ⁻¹]	$1.08 \cdot 10^9$	$4.425 \cdot 10^8$
m [°C wt% ⁻¹]	2.5	2.2
ϑ_0 [°C]	660	505
ν [m ² s ⁻¹]	$5 \cdot 10^{-7}$	$8 \cdot 10^{-7}$
κ_l [m ² s ⁻¹]	10^{-6}	10^{-8}
d_0 [m]	10^{-9}	$5 \cdot 10^{-12}$
k	0.17	0.0656
α	0.03	0.03
n	4	4
A_4	1	1
σ_{04}	40	70

The opposite is also possible (outgoing flow). At $\omega < 0$, the concentration of impurities is lower compared to the red curve. The outgoing flow washes out copper, lowering the concentration inside the two-phase zone. The liquid flow can act in both directions, increasing or decreasing the concentration of impurities. The results obtained are consistent with the phase field calculations of dendritic crystallization performed in Refs. (Deguen et al. 2007).

We also compare expression (20) for the concentration of impurities with the experimental data. The lines differ as a result of various initial conditions and concentrations. The solid lines describe the current theory with a flow. The dashed lines describe the theory without a flow, the Brody–Flemings solution. As follows from the graph, both solid curves agree with the experimental data much better than the solutions without a flow. Although the flow was assumed to be weak, the differences are significant.

During solidification, the dendritic mushy zone can be considered as a permeable medium for a fluid flow. Permeability is defined as a quantitative parameter indicating how difficult it is for the fluid to pass through the mushy zone. Fig. 3a shows a plot of permeability K versus solid phase portion φ , calculated using the formula:

$$K(\varphi) = K_0 (1 - \varphi)^3, \quad (24)$$

where K_0 is the permeability at $\varphi = 0$. Next, we compare expression (24) for permeability with the experimental data; as we can see from the graph, the curve agrees well with the experimental data. Fig. 3b shows the dependence of permeability K on the coordinate x at different flow velocities; expressions (21), (22), and (24) were used to plot this dependence. The graph shows that for an incoming flow $\omega > 0$, the permeability of the two-phase region is lower than the permeability in the absence of a flow. This is due to the absorption of impurities brought about by the flow by growing dendrites, due to which the volume of the solid phase in the two-phase region increases and the permeability decreases.

The situation with the outgoing flow, at $\omega < 0$, is associated with a decrease in the concentration of impurities due to their washing by the outflow, which leads to a decrease in the volume of the solid material in the two-phase region and an increase in its permeability.

During the solidification process, the microstructural characteristics are influenced by various quantities: the portion of the solid phase φ , the impurity concentration at given temperature gradients g_s and g_l , and consequently the crystallization rate ν , which is determined by the temperature gradients, equation (17), as well as the flow rate u . As a microstructural parameter, we will consider the interdendritic distance λ_1 . Considering the axisymmetric shape of the dendrites, we have the expression for the interdendritic distance in the following form (Quaresma et al. 2000):

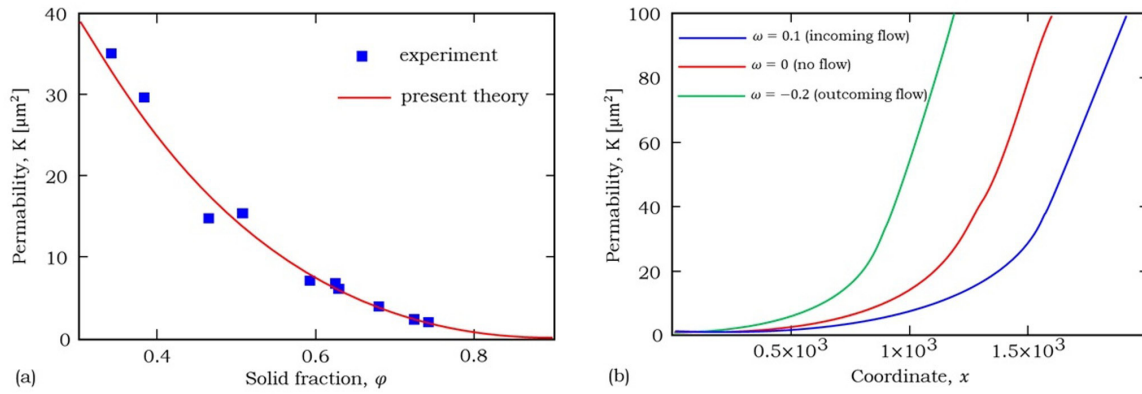


Fig. 3. (a) The permeability of the two-phase region (24) is compared with the experimental data (Murakami et al. 1984) (blue squares). (b) The permeability of the two-phase region for different convective flows: $\omega = 0.1$ (incoming flow, as shown in Fig. 1), $\omega = 0$ (stagnant melt), and $\omega = -0.2$ (outcoming flow); the physical parameters of the Al–Cu melt are presented in Table 1 with $\sigma_{\infty} = 5 \text{ wt\%}$, $g_s = 5 \cdot 10^2 \text{ }^\circ\text{C m}^{-1}$, $g_l = 10^2 \text{ }^\circ\text{C m}^{-1}$

$$\lambda_1 = \sqrt{\frac{2\pi p}{q(\partial\phi/\partial\zeta)}}, \zeta = v\tau, \quad (25)$$

where p is the diameter of the dendrite tip, $q = 1$ and $q = 0.86$ for cubic and hexagonal dendritic arrays, respectively.

Taking into account the moving frame of reference, we can rewrite equation (25) for the interdendritic distance, which describes the stationary crystallization process with a quasi-equilibrium two-phase layer, in the following form:

$$\lambda_1(v, u) = \sqrt{\frac{2\pi D_l p(v, u)}{qv} \frac{dx}{d\phi}}, x = \varepsilon, \phi = \phi_*, \quad (26)$$

at the boundary between the purely solid phase and the two-phase region, where $\phi = \phi_*$, $dx/d\phi$ is determined by expression (21) and takes the form

$$\frac{dx}{d\phi} = -\frac{P\Lambda_0(\phi_*)}{\phi_* + PG_l\Lambda_1} \frac{dC}{d\phi}, \phi = \phi_*,$$

where $dC/d\phi$ is from expression (20). In this case, the diameter of the dendrite tip p is determined by the theory of stable growth of dendrites

$$\frac{2d_0\kappa_l}{p^2v} = \sigma_*(p, v, u), \phi = \phi_*, \quad (27)$$

where d_0 is the capillary length and σ_* is a function of p , v , and u given in Appendix A. The selection criterion (27) for stable dendritic growth is a nonlinear equation to determine the dendrite tip diameter p as a function of the solidification rate v and the flow rate u . By substituting $p(v, u)$ into (26), we obtain the primary interdendritic distance as a function of velocity and flow rate $\lambda_1 = \lambda_1(v, u)$.

Fig. 4 shows the dependence of the interdendritic distance on the crystallization rate, according to equation (25). The graph represents three experiments with binary melts. The purple squares represent the aluminum-copper melt with a constant inflow of $\omega = -2$. The orange circles and pink diamonds represent the Sn-5wt%Pb and Sn-2.5wt%Pb melts, respectively. In the case of tin-lead melts, the convective currents in the liquid are minimized, so the flow velocity in the liquid phase is $\omega = 0$. All curves lie within the experimental data and are consistent, taking into account the experimental error.

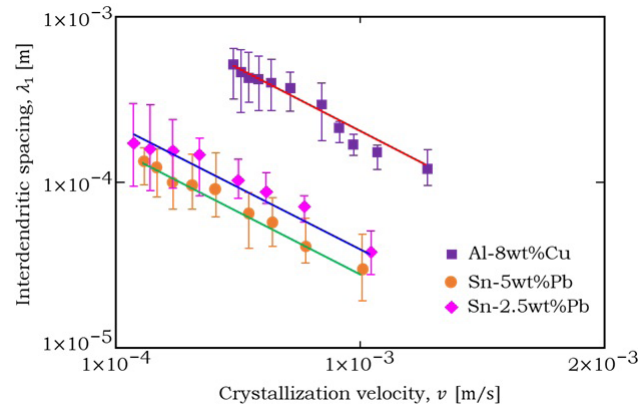


Fig. 4. Primary interdendritic distance λ_1 as a function of crystallization rate v . The theory (expressions (25)–(27), red line for Al–Cu ($\sigma_{iso} = 8$ wt%), blue line for Sn–Pb ($\sigma_{iso} = 2.5$ wt%), green line for Sn–Pb ($\sigma_{iso} = 5$ wt%)) is compared with experimental data for Al–Cu (Barros et al. 2015) and Sn–Pb (Rocha et al. 2003) melts. The physical parameters for the melts are given in Table 1 with $g_s = 140^\circ\text{C m}^{-1}$, $g_l = 45^\circ\text{C m}^{-1}$, $b = 0.5$, $\alpha_d = 0.8$ for Al-8wt%Cu; $g_s = 90^\circ\text{C m}^{-1}$, $g_l = 20^\circ\text{C m}^{-1}$, $b = 0.7$, $\alpha_d = 2.9$ for Sn-5wt%Pb; $g_s = 90^\circ\text{C m}^{-1}$, $g_l = 20^\circ\text{C m}^{-1}$, $b = 0.8$, $\alpha_d = 0.8$ for Sn-2.5wt%Pb

Conclusions

This paper presents a theory describing the crystallization process with a two-phase region. The model also takes into account weak inflow and outflow currents. To find solutions, relaxation times of temperature and concentration fields were considered, on the basis of which some estimates were made to simplify the model. The heat and mass transfer equations were then integrated, taking into account the fixed temperature gradients in the solid and liquid phases, to determine the solidification rate. This solidification rate of the two-phase layer coincides with the rate of directed solidification with a flat solid–liquid interface.

It is important to note that an extension of the Scheil–Brody–Flemings law was derived. This law allows one to determine the impurity concentration in a two-phase layer as a function of the solid phase portion for the steady-state solidification scenario. The law takes into account the effects of back diffusion and weak convection in the two-phase layer. This law has the form of an exact solution to the heat and mass transfer equations for the process described above. In this paper, the following parameters were also analytically determined: impurity concentration, temperature, and solid phase fraction in the two-phase region, as well as the impurity concentration in the liquid. The thickness of the two-phase region was determined and, by combining theory with the selection criterion, a relationship was found for the interdendritic distance.

To test the theory developed, some comparisons with experiments were conducted. Figs. 2 and 3 show the dependence of concentration on the solid phase fraction and the dependence of permeability on the coordinate, respectively. The graphs present data with different values of the incoming and outgoing fluxes. In each case, it is clear that even the weak flow influences the crystallization process, and the agreement is much better when the weak flow is taken into account. Fig. 4 shows the dependence of interdendritic spacing on the crystallization rate. The dependence is plotted for three binary melts; in all the three cases, there is good agreement with the experimental data.

The method developed in this paper can be applied to the solution of the problem of non-stationary crystallization with a two-phase region in the presence of weak convection in the liquid phase. Such a theory can be developed on the basis of the mathematical algorithm described in detail in Refs. (Alexandrov et al. 2008; Alexandrov, Nizovtseva 2008b; Galenko et al. 2024). Another direction of research is the theory of combined directional and volumetric crystallization, taking into account the slow flow, both outgoing and incoming. Such a problem can be considered in conjunction with theories of volumetric and directed crystallization (Alexandrov, Britousova 2015; Alexandrov, Galenko 2017; Makoveeva, Alexandrov 2024).

Appendices A: Selection criterion of stable dendritic growth

Considering crystal growth in the case of weak forced convection, one can derive the following criterion of stable growth for a dendrite tip, which connects the tip diameter p , tip velocity v , and velocity u of the fluid flow as follows (Galenko et al. 2024):

$$\sigma_*(p, v, u) = \frac{\sigma_{0n} \alpha_d^{7/n} A_n^{7/n}}{1 + b \tau_n^{v_n}} \cdot \left[\frac{1}{(1 + a_{1n} \alpha_d^{2/n} A_n^{2/n} P_g)^2} + \frac{2m\sigma_i(1-k)\lambda_l}{(1 + a_{2n} \alpha_d^{2/n} A_n^{2/n} P_c)^2 L_v D_l} \right], \quad (28)$$

where

$$\begin{aligned} A_n &= 2^{-3n/4} \sum_{k=0}^n \binom{n}{k} i^{n-k} \cos \frac{(n-k)\pi}{2}, \\ \tau_n &= \alpha_d^{-3/n} A_n^{-3/n} \frac{a u d_0}{4 p v P} \left(1 + \frac{2\kappa_l}{D_l} \right), \\ v_n &= \frac{n+7}{2(n+3)}, P = 1 + \frac{2m\sigma_i(1-k)\lambda_l}{L_v D_l}, \\ a &= \begin{cases} \sqrt{\frac{Re \exp(-Re/2)}{2\pi \operatorname{erfc}(\sqrt{Re}/2)}}, & \text{2D case,} \\ \frac{\exp(-Re/2)}{E_1(Re/2)}, & \text{3D case,} \end{cases} \\ E_1(y) &= \int_y^\infty \frac{\exp(-x)}{x} dx, a_{2n} = \sqrt{2} a_{1n}, \\ a_{1n} &= \sqrt{\frac{8\sigma_{0n}}{7} \left(\frac{3}{56} \right)^{3/8}} A_n^{3/(2n)} \alpha_d^{(12-3n)/(8n)}, \end{aligned}$$

$P_g = pv/(2\kappa_l)$ and $P_c = pv/(2D_l)$ are the growth and chemical Péclet numbers, $Re = pu/v$ is the Reynolds number, ν is the kinematic viscosity, n is the order of crystalline symmetry ($n = 4$ for rectangles, $n = 6$ for ice crystals and snowflakes; see Ref. (Alexandrov, Galenko 2017.) for more details), σ_{0n} and b are the selection constants, α_d is the anisotropy constant, d_0 is the capillary constant, and $\sigma_i = \sigma_{i\infty} C(\varphi)$.

Substitution of σ_* from (28) into (27) leads to a single non-linear equation for $p(v, u)$. Note that this equation can be solved analytically in the case of small solidification velocities in the absence of convection (for details, see Refs. (Alexandrov, Britousova 2015; Makoveeva, Alexandrov 2024)).

Conflict of Interest

The author declares that there is no conflict of interest, either existing or potential.

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Beyond the standard quantum Zeno effect

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Abstract. In this paper, we introduce a functional for the decoherence rate of a quantum system. The quantum system is modeled as a qubit that can be in the state $|1\rangle$, $|0\rangle$, or in a superposition. In addition to external dephasing and the Zeno attenuation rate acting on the quantum system, resource losses of the measuring channel are taken into account. It is shown that for the parameters corresponding to the limit of ideally frequent measurements in the quantum Zeno effect, the stability of the qubit state is not increased. The existence of optimal values of the measurement time interval and the measurement imperfection parameter is established; at these values, the decoherence rate of the qubit state reaches a minimum. Calculations show that in the case under consideration, the qubit coherence time increases by a factor of 11.5, which ensures an increase in the stability of the qubit state.

Keywords: stability, qubit, quantum Zeno effect, minimum, measurement imperfection, stability principle

Introduction

Decoherence limits the efficiency of quantum systems by affecting the quantum state. One approach to increasing the stability of a quantum system (Sokolovski et al. 2012) is to use the quantum Zeno effect, which involves suppressing its evolution through a sequence of frequent ideal measurements. This effect was first theoretically predicted in (Khalfin 1968) and subsequently received experimental confirmation in various physical systems (Itano et al. 1991; Misra, Sudarshan 1977).

As part of the proposed model, which takes into account resource losses of the measuring channel, the functional of the total decoherence rate diverges in the limit of ideally frequent measurements. The stability principle (Kamalov 2025; 2026) is based on the requirement that the first variation of a functional is zero and the second variation is positive. This principle characterizes the stability of quantum-system states with respect to small perturbations.

The stability principle is applied here to the functional of the total decoherence rate, which acts as an action analogue for the process of measuring the state of a quantum system. The aim of this work is to analyze how the measurement imperfection parameter affects the stability of a quantum system against decoherence.

Model and functional of decoherence rate

Qubit: quantum Zeno effect and imperfect measurements

The quantum system under consideration is a qubit, which can be in the state $|1\rangle$, $|0\rangle$, or in a superposition. The Hamiltonian H describes the evolution of the quantum state of a qubit:

$$H = \frac{\hbar\Omega}{2} \sigma_x,$$

where Ω is Rabi frequency, and σ_x — Pauli matrix operator.

The evolution of the quantum state of a qubit over a measurement time interval τ is described by a unitary operator $U(\tau) = \exp(-iH\tau)$. We assume that at the initial moment of time, the qubit is in the state $|0\rangle$:

$$|\psi(0)\rangle = |0\rangle.$$

The state of the qubit $|\psi(\tau)\rangle$ over an interval τ at $\hbar = 1$ is determined as follows:

$$|\psi(\tau)\rangle = \cos \frac{\Omega\tau}{2} |0\rangle - i \sin \frac{\Omega\tau}{2} |1\rangle.$$

The probability of detecting $P_{|0\rangle}(\tau)$ a qubit in the initial state:

$$\begin{aligned} P_{|0\rangle}(\tau) &= |\langle 0|\psi(\tau)\rangle|^2 \\ P_{|0\rangle}(\tau) &= \cos^2 \frac{\Omega\tau}{2}. \end{aligned}$$

For infinitesimal functions:

$$\cos^2 \frac{\Omega\tau}{2} \cong 1 - \frac{\Omega^2\tau^2}{4} + O(\tau^4). \quad (1)$$

Let us write the expression for $P_{|0\rangle}(\tau)$ taking into account (1):

$$P_{|0\rangle}(\tau) \cong 1 - \frac{\Omega^2\tau^2}{4}.$$

Let $N = t/\tau$ consecutive measurements be performed during time t . Then the probability that the qubit will remain in the initial state is $|0\rangle$:

$$P_{|0\rangle}(\tau) \cong \left(1 - \frac{\Omega^2\tau^2}{4}\right)^N.$$

The expression for the probability of a qubit remaining in its initial state $P_{|0\rangle}(t)$ is defined as:

$$P_{|0\rangle}(t) \cong \exp\left(-\frac{\Omega^2\tau}{4}t\right).$$

Thus, the expression for the Zeno attenuation rate is written as:

$$\gamma_Z(\tau) \approx \frac{\Omega^2}{4} \tau.$$

We introduce the parameter $\lambda \in (0,1)$, which characterizes measurement imperfection. Physically, it reflects the limitations of the measurement setup (for example, the finite efficiency of the detector). As λ decreases, the efficiency of the measuring channel diminishes, which leads to an increase in the interval between successive measurements to a value τ/λ :

$$\gamma_z(\tau, \lambda) \approx \frac{\Omega^2 \tau}{4 \lambda}. \quad (2)$$

As $\lambda \rightarrow 1$ expression (2) tends to the standard quantum Zeno-effect form. This parameterization is not a universal law of quantum measurements and is used as a simple phenomenological model of the influence of limited resources of measuring devices on the dynamics of a quantum system. In addition to the Zeno slowing of the quantum system's state, the system is subject to external dephasing γ . Further analysis of the model under study compares the characteristic frequency Ω with external dephasing:

$$\Omega \approx \gamma. \quad (3)$$

Approximation (3) simplifies analytical and numerical estimates of the qubit state coherence time. The model assumes that qubit state measurements are accompanied by resource losses. These losses are introduced as an additional channel to qubit state decoherence, competing with both Zeno slowdown and external dephasing.

Resource losses of the measuring channel

To take into account the resource losses of the measuring channel with the measurement imperfection parameter, the following dependence is used:

$$\beta(\lambda) = \beta_0 \frac{1+\lambda}{(1-\lambda)^p},$$

where β_0 is a positive constant and $p > 0$ characterizes the rate of growth of losses in the measuring channel.

The proposed dependence is determined by the following factors:

- When the parameter λ decreases, the resource losses of the measuring channel tend to a certain value ($\beta(\lambda \rightarrow 0) \rightarrow \beta_0$);
- When the ideal projective measurement regime is approached, the resources of the measuring channel increase without the ($\beta(\lambda \rightarrow 1) \rightarrow \infty$) limit. This leads to an increase in the system's sensitivity to hardware limitations.

The chosen form of the $\beta(\lambda)$ dependence is a phenomenological coarse-grained description of measurement-channel losses and is consistent with the general conclusion of works (Deffner et al. 2016; Guryanova et al. 2020) about the unlimited growth of resource costs when approaching ideal measurements. It may describe, for example, finite detector efficiency, detector dead time, classical processing overhead, heating, and back-action costs that increase when the measurement becomes closer to an ideal projective one. This dependence is not derived from a specific microscopic detector model; therefore, the main conclusion of this work is not tied to a unique form of $\beta(\lambda)$ but to the competition between Zeno suppression of dynamics and the growth of the resource losses of the measuring channel.

Full loss-rate functional (action analogue)

The decoherence rate of the qubit state consists of external dephasing, the Zeno term, and the resource losses of the measuring channel, normalized to τ . For the model under consideration, we will take the value $p = 3/2$:

$$G(\tau, \lambda) = \gamma + \gamma_z(\tau, \lambda) + \frac{\beta(\lambda)}{\tau} = \gamma + \frac{\Omega^2 \tau}{4 \lambda} + \frac{\beta_0}{\tau} \frac{1+\lambda}{(1-\lambda)^{3/2}}. \quad (4)$$

For the standard quantum Zeno effect ($\tau \rightarrow 0, \lambda \rightarrow 1$) the functional (4) diverges. As part of further analysis, in the model under consideration, the coherence of a quantum system decreases according to the law $\exp(-Gt)$, with the conservation of coherence time defined as $\sim 1/G$. The stability of the quantum state of a qubit corresponds to the minimum of G . Thus, the functional of the total decoherence rate can be considered as an analogue of the action in the problem of optimizing quantum measurements.

Unlike the standard principle of least action, it is not the path integral of the system that is minimized, but rather the functional of the total decoherence rate. The minimum of the functional $G(\tau, \lambda)$ corresponds to the following:

$$\delta G(\tau, \lambda) = 0, \delta^2 G(\tau, \lambda) > 0,$$

where δ is the variation of the functional.

We will now analyze the minimization of the functional of the decoherence rate of the qubit state.

Minimization of the functional

First variation

For a fixed parameter λ , we calculate the first variation, that is, the partial derivative of the functional $G(\tau, \lambda)$ with respect to τ :

$$\begin{aligned} \frac{\partial G(\tau, \lambda)}{\partial \tau} &= \frac{\Omega^2}{4} \frac{1}{\lambda} - \frac{\beta_0}{\tau^2} \frac{1+\lambda}{(1-\lambda)^{\frac{3}{2}}}, \\ \frac{\Omega^2}{4} \frac{1}{\lambda} - \frac{\beta_0}{\tau^2} \frac{1+\lambda}{(1-\lambda)^{\frac{3}{2}}} &= 0 \Rightarrow \tau_{\text{opt}}^2 = \frac{4\beta_0\lambda}{\Omega^2} \frac{1+\lambda}{(1-\lambda)^{\frac{3}{2}}}. \end{aligned} \quad (5)$$

Equation (5) yields the expression for τ_{opt} . Similarly, we find the partial derivative of the functional $G(\tau, \lambda)$ with respect to λ :

$$\frac{\partial G(\tau, \lambda)}{\partial \lambda} = -\frac{\Omega^2}{4} \frac{\tau}{\lambda^2} + \frac{\beta_0}{\tau} \frac{5+\lambda}{2(1-\lambda)^{\frac{5}{2}}} = 0. \quad (6)$$

Multiplying both parts of equation (6) by 2τ , we obtain:

$$\frac{\Omega^2}{2} \frac{\tau^2}{\lambda^2} = \beta_0 \frac{5+\lambda}{(1-\lambda)^{\frac{5}{2}}}. \quad (7)$$

We substitute τ_{opt}^2 into expression (7):

$$\frac{2\beta_0}{\lambda} \frac{1+\lambda}{(1-\lambda)^{\frac{3}{2}}} = \beta_0 \frac{5+\lambda}{(1-\lambda)^{\frac{5}{2}}}. \quad (8)$$

After mathematical transformations of expression (8), we obtain the following:

$$\frac{5+\lambda}{(1-\lambda)^{\frac{5}{2}}} = \frac{2(1+\lambda)}{\lambda(1-\lambda)^{\frac{3}{2}}}. \quad (9)$$

Expression (9) is transformed into a quadratic equation:

$$3\lambda^2 + 5\lambda - 2 = 0. \quad (10)$$

The numerical solution of equation (10) leads to a positive root $\lambda_{\text{opt}} = \frac{1}{3}$ at τ_{opt} :

$$\tau_{\text{opt}} = \frac{2}{\Omega} \sqrt{\beta_0 \lambda \frac{1+\lambda}{(1-\lambda)^{\frac{3}{2}}}}.$$

The obtained values were verified using the built-in Given–Find tool for solving nonlinear equations in the Mathcad environment.

The accuracy of calculations in Given–Find is determined by the variables α and μ . The variable α determines the absolute error of the calculation. For the equation $f(x) = g(x)$ the solution is considered found if the following condition is met:

$$|f(x) - g(x)| \leq \alpha.$$

The variable μ (convergence tolerance) controls the criterion of the iterative process:

$$\frac{|x_{k+1} - x_k|}{x_{k+1}} \leq \mu,$$

where k is the step between iterations, and x_k is the root of the equation at the k^{th} step.

When solving expression (4), the following values were used: $\gamma = 1$, $\Omega = 1$, $\beta_0 = 0.5$, $\alpha = \mu = 10^{-3}$. For the initial approximation, the values were as follows: $\tau = 1$, $\lambda = 1$. The values of these parameters were selected for a qualitative analysis of the functional under consideration. To improve reproducibility, several initial approximations in the domain $\tau > 0$ and $0 < \lambda < 1$ were tested. The iteration converged to the same positive stationary point, whereas nonphysical roots with λ outside the admissible interval or $\tau \leq 0$ were discarded.

Among the obtained solutions, the positive roots have physical meaning: $\tau_{\text{opt}} = 1.278$ and $\lambda_{\text{opt}} = \frac{1}{3}$. The minimum of the functional for τ_{opt} and λ_{opt} corresponds to the value $G(\tau_{\text{opt}}, \lambda_{\text{opt}}) \cong 2.917$. The solution is stable under variations of the initial approximations, which indicates the existence of a single physically significant minimum in the region $0 < \lambda < 1$. Fig. 1 shows the dependence of the functional $G(\tau, \lambda)$ on the parameters τ and λ .

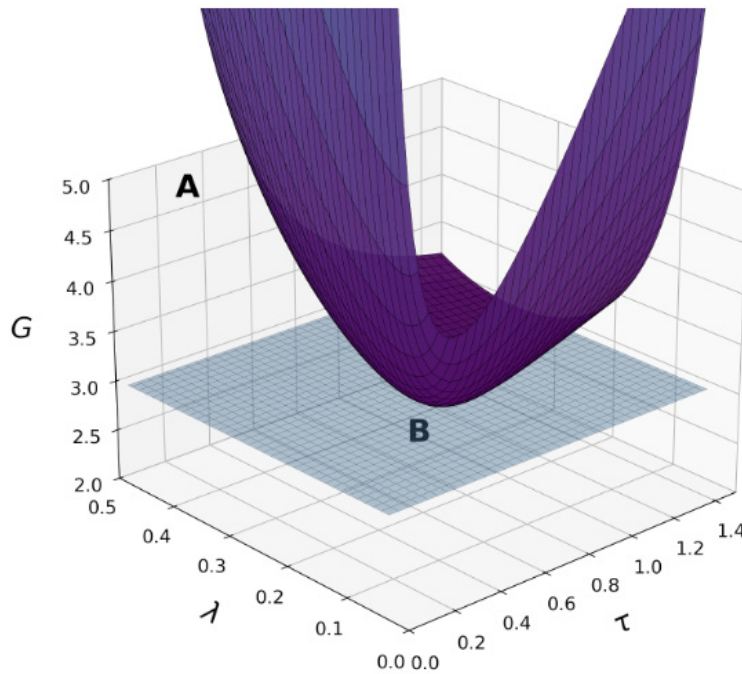


Fig. 1. A — dependence of the functional G on the measurement time interval τ and the measurement imperfection λ . B — level plane corresponding to the minimum of the functional

Thus, the analysis of the obtained results shows that the values τ_{opt} and λ_{opt} actually correspond to the minimum of the functional G .

Check of the second variation

According to the stability principle, the second variation of the functional must be positive. The second derivatives have the form:

$$\begin{aligned}\frac{\partial^2 G(\tau, \lambda)}{\partial \tau^2} &= \frac{\beta_0}{\tau^3} \frac{1+\lambda}{(1-\lambda)^{3/2}} > 0 \\ \frac{\partial^2 G(\tau, \lambda)}{\partial \lambda^2} &= \frac{\Omega^2}{2} \frac{\tau}{\lambda^3} + \frac{\beta_0}{\tau} \frac{3(9+\lambda)}{4(1-\lambda)^2} > 0.\end{aligned}\quad (11)$$

The result (11) indicates that the presence of a minimum of the functional $G(\tau, \lambda)$ acts as a criterion for the stability of the quantum state of the qubit.

Comparison with near-perfect measurements

Functional (4) for the value τ_{opt} corresponds to the following expression:

$$G_{\min}(\lambda)|_{\tau_{\text{opt}}} = \gamma + \frac{\Omega^2}{4} \frac{1}{\lambda} \frac{2\sqrt{\lambda\beta(\lambda)}}{\Omega} + \beta(\lambda) \frac{1+\lambda}{2\sqrt{\lambda\beta(\lambda)}}.$$

After the transformation $G_{\min}(\lambda)|_{\tau_{\text{opt}}}$ we arrive at the following:

$$G_{\min}(\lambda)|_{\tau_{\text{opt}}} \cong \gamma + \Omega \sqrt{\frac{\beta(\lambda)}{\lambda}}. \quad (12)$$

Expression (12) is interpreted as the minimum decoherence rate achieved at the optimal measurement frequency.

In the limit $\lambda_{\text{im}} \rightarrow 1$ (ideal measurements), expression (12) takes the following form:

$$G_{\min}(\lambda_{\text{im}}) = \gamma + \Omega \sqrt{\frac{\beta_0}{\lambda} \frac{1+\lambda}{(1-\lambda)^{3/2}}} \approx \gamma + 45 \cdot \Omega \sqrt{\beta_0}.$$

When $\lambda_{\text{opt}} = 1/3$, expression (12) is simplified to the following form:

$$G_{\min}(\lambda_{\text{opt}}) = \gamma + \Omega \sqrt{\frac{\beta_0}{\lambda} \frac{1+\lambda}{(1-\lambda)^{3/2}}} \approx \gamma + 3 \cdot \Omega \sqrt{\beta_0}.$$

Using relation (3), we write the following:

$$\frac{G_{\min}(\lambda_{\text{im}})}{G_{\min}(\lambda_{\text{opt}})} \approx \frac{46 \cdot \Omega \sqrt{\beta_0}}{4 \cdot \Omega \sqrt{\beta_0}} \approx 11.5. \quad (13)$$

Expression (13) indicates that, for the selected set of parameters, the qubit coherence time increases by a factor of 11.5 compared with the ideal-measurement limit. This estimate is not a universal constant: it is determined by the chosen values of γ , Ω , and β_0 , and must be recalculated when these physical scales change.

Discussion of the results

Within the model in question, the value $\lambda_{\text{opt}} = 1/3$ indicates that the minimum of the qubit decoherence-rate functional is achieved at a finite value of the measurement imperfection parameter. Thus, in this model, imperfect measurements can be more favorable than the ideal-measurement limit for stabilizing the qubit state. The conclusion is model-dependent and should not be interpreted as a universal statement for all quantum-measurement schemes. The sensitivity to the exponent p in the loss term was also analyzed. If p is left arbitrary in $\beta(\lambda)$, minimization over λ leads to the condition $p\lambda^2 + (1+p)\lambda - 1 = 0$. Therefore, for $p > 0$ the optimal value of λ remains finite and lies in the interval $0 < \lambda < 1$. Changing p shifts the position of the minimum and the numerical gain in coherence time, but does not remove the finite optimum as long as the measurement-channel losses grow when the ideal-projective-measurement limit is approached. The value $p = 3/2$ is therefore used as a representative model case rather than as a universal exponent.

In contrast to the works (Belan, Parfenyev 2020; Hacohen-Gourgy, Martin 2020; Jacobs, Steck 2006), which investigate optimal modes of Zeno quantum dynamics and methods of continuous quantum monitoring, the present work optimizes the stability of a quantum system simultaneously with respect to the measurement time interval and the measurement imperfection parameter. Thus, the measurement imperfection parameter can be included among the control parameters of quantum control in real experimental setups, where ideal measurements are limited by the finite characteristics of measuring devices. Promising directions for further research include:

- Derivation of loss functional from microscopic models of detectors;
- Numerical simulation of open quantum systems;
- Analysis of different noise statistics and detector-feedback mechanisms;
- Analysis of multi-qubit systems.

The main result of the work is the demonstration of competition between Zeno suppression of dynamics and the resource costs of the measuring channel. The conclusion is expected to remain valid in regimes where environmental noise can be represented as an additional positive decoherence channel and where measurement resources grow strongly near the ideal projective-measurement limit.

Strongly non-Markovian noise, correlated detector back-action, feedback from the measuring device, or multi-qubit interactions may quantitatively change the position of the minimum and, in some architectures, modify the stability criterion itself. In such cases, the optimum must be recalculated for the specific experimental platform.

Thus, the obtained result should be considered as a model demonstration that finite measurement imperfection can increase the stability of the qubit state under realistic resource constraints.

Conclusions

In this paper, we introduced a functional for the decoherence rate of a qubit state, optimizing it with respect to the measurement time interval and the measurement imperfection parameter. As part of the studied model, the stability principle is used as an optimization criterion.

The obtained results are consistent with what is observed in quantum measurement theory: achieving the most ideal measurements is accompanied by increased resource consumption. In the model under consideration, this leads to a tradeoff between the effectiveness of Zeno's dynamic suppression and the losses in the measurement channel.

Calculations show that, for the selected set of parameters, the optimal measurement mode results in an 11.5-fold increase in coherence time compared with the ideal-measurement limit. This value is illustrative and depends on the physical scales of the model. The results indicate that finite measurement imperfection can be used as a control parameter for increasing the stability of the qubit state.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

Timur F. Kamalov developed a methodology for analyzing the stability principle of a qubit and provided guidance for writing the manuscript; Andrey A. Borisov and Anton A. Borisov formulated the physical problem and conducted numerical calculations.

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Account of asymptotic couplings in collisional dynamics of H_2 quasimolecule

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Abstract. This work studies mutual neutralization processes in $H^- + H^+$ collisions using the reprojection method within the Born–Oppenheimer approach. This method enables nuclear dynamical calculations with non-vanishing radial couplings at large internuclear distances. Such calculations were performed for a mixed basis set of $^1\Sigma_g$ and $^1\Sigma_u$ molecular states with radial coupling matrix elements with analytically calculated asymptotic values. The partial mutual neutralization cross sections are calculated for a collision energy range from 0.001 to 100 eV.

Keywords: inelastic processes, nonadiabatic transitions, asymptotic couplings, mutual neutralization, cross sections, hydrogen

Introduction

The study of inelastic processes in collisions of hydrogen negative and positive ions is instrumental in analyzing the simplest electron transfer process in atomic collisions. Theoretical investigations into $H^- + H^+$ collisions are challenged by additional symmetry connected with the reflection of nuclei. This collisional system has scattering states of $^1\Sigma_g$ and $^1\Sigma_u$ molecular symmetries, and previous theoretical studies (Hörnquist et al. 2022; Nkambule et al. 2016; Stenrup et al. 2009) performed separate sets of calculations within each one of them. However, our analytical calculations show that several molecular states of different parity are coupled at large internuclear distances. Non-vanishing coupling matrix elements are fundamental to the Born–Oppenheimer approach, that is also called the electron translation problem, as non-adiabatic couplings in the asymptotic region induce transitions between different electronic molecular states at large internuclear distances. To solve this problem, the reprojection method was proposed in (Belyaev 2010) and later in (Yakovlev et al. 2018). However, it was used mostly in heteronuclear systems, and one study (Hedvall et al. 2024) applied the reprojection method to collisions of the same nuclei, namely $H^- + H^+$; nuclear dynamics was also treated separately for $^1\Sigma_g$ and $^1\Sigma_u$ states. This work aims to include the asymptotic values of radial couplings between $^1\Sigma_g$ and $^1\Sigma_u$ molecular states in calculations of non-adiabatic nuclear dynamics.

Theory

Mutual neutralization processes in $H^- + H^+$ collisions are investigated within the Born–Oppenheimer approach that divides the problem into two parts: electronic structure calculations and non-adiabatic nuclear dynamics study. The electronic structure of the H_2 quasimolecule is calculated in (Stenrup et al. 2009) and has information on adiabatic potential energies U_j and radial coupling matrix elements $\left\langle \varphi_j \left| \frac{\partial}{\partial R} \right| \varphi_k \right\rangle$ as functions of internuclear distance R . Nuclear dynamics study focuses on solving the coupled channel equations system:

$$\begin{aligned} & \left(-\frac{\hbar^2}{2M} \frac{\partial^2}{\partial R^2} + \frac{\hbar^2 J(J+1)}{2M R^2} + U_j(R) - E \right) F_j = \\ & = \frac{\hbar^2}{M} \sum_{k \neq j} \left\langle \varphi_j \left| \frac{\partial}{\partial R} \right| \varphi_k \right\rangle \frac{\partial F_k}{\partial R} + \frac{\hbar^2}{2M} \sum_k \left\langle \varphi_j \left| \frac{\partial^2}{\partial R^2} \right| \varphi_k \right\rangle F_k, \end{aligned} \quad (1)$$

where M — reduced mass of nuclei, J — total angular momentum quantum number, E — total energy, and F_j — radial wave functions of nuclei. Numerical solution of these equations gives matrix $\underline{\underline{R}}$, which can be used to calculate scattering matrix $\underline{\underline{S}}$ and transition probabilities and inelastic cross sections

$$\underline{\underline{S}} = (-1)^J \exp(-i\underline{\underline{K}}R_0) \underline{\underline{K}}^{-\frac{1}{2}} \left(\underline{\underline{t}}^- + i\underline{\underline{R}}\underline{\underline{t}}^-\underline{\underline{K}} \right) \left(\underline{\underline{t}}^+ + i\underline{\underline{R}}\underline{\underline{t}}^+\underline{\underline{K}} \right)^{-1} \underline{\underline{K}}^{\frac{1}{2}} \exp(-i\underline{\underline{K}}R_0), \quad (2)$$

where matrices $\underline{\underline{t}}^\pm$ are introduced in the reprojection method (Belyaev 2010; 2022) as follows

$$t_{kj}^\pm = \delta_{kj} \pm \frac{iK_j \hbar^2}{M(U_k(\infty) - U_j(\infty))} \left\langle \varphi_j \left| \frac{\partial}{\partial R} \right| \varphi_k \right\rangle_\infty, \quad (3)$$

and take into account that incoming and outgoing waves in a single atomic state must be distributed among all molecular states in the asymptotic region. Non-vanishing radial matrix elements at large internuclear distances arise since electronic structure calculations are usually performed in molecular coordinates. In the standard Born–Oppenheimer approach, asymptotic values of radial coupling matrix elements are neglected, which corresponds to setting $\underline{\underline{t}}^\pm$ to a unity matrix in equation (2).

Asymptotic values of radial coupling matrix elements can be calculated using asymptotic wave functions for different scattering states of the H_2 quasimolecule. At large internuclear distances, radial couplings can be expressed via atomic transition dipole matrix elements

$$\left\langle \varphi_j \left| \frac{\partial}{\partial R} \right| \varphi_k \right\rangle_\infty = \gamma_k \frac{m}{\hbar^2} [U_j(\infty) - U_k(\infty)] \langle \varphi_j | z^{at} | \varphi_k \rangle_\infty, \quad (4)$$

where $U(\infty)$ is the asymptotic value of adiabatic potential energy, m — reduced mass of the electron and the nuclei, and factor $\gamma_k = M_{a,b}/(M_a + M_b)$ for nuclei a and b , which for the case of the H_2 quasimolecule has value $\gamma_k = 1/2$. Equation (4) shows that some of the matrix elements have zero values: these are matrix elements that correspond to transitions between degenerate states ($U_j(\infty) = U_k(\infty)$), between states where dipole transition is forbidden, and between covalent and ionic states.

Electronic structure

Calculations for the electronic structure of the H_2 quasimolecule that includes adiabatic potentials and coupling matrix elements for 13 scattering channels were presented in (Stenrup et al. 2009). This work was followed by (Hörnquist et al. 2022), with several higher-lying states added; however, they showed that cross sections to the scattering states $H(1s)+H(4l)$ are negligible. Ionic state $H^-(1s^2) + H^+$ produces $^1\Sigma_g$ and $^1\Sigma_u$ molecular symmetry, where subscripts g and u denote even and odd wave functions with respect to the reflection of nuclei. In our work we consider seven scattering states of $^1\Sigma_g$ molecular symmetry and six scattering states of $^1\Sigma_u$ symmetry, with each symmetry including one

ionic state. Scattering channels, their molecular terms, and asymptotic energies measured from the ground state are collected in Table 1. Adiabatic potential energies as functions of the internuclear distance R are shown in Fig. 1, with solid lines representing $^1\Sigma_g$ states and dashed lines — $^1\Sigma_u$ states. Table 1 and Fig. 1 demonstrate that scattering channels $H(1s)+H(nl)$ that have the same quantum number n are asymptotically degenerate, as well as two ionic states.

Table 1. Scattering channels for $H(1s) + H(nl)$ and $H^-(1s^2) + H^+$ that form $^1\Sigma_{g,u}$ molecular symmetry and their asymptotic energies with respect to the ground state

j	Scattering channel	Term	Asymptotic energy, a. u.
1	$H(1s) + H(1s)$	$1\ ^1\Sigma_g$	0.0
2	$H(1s) + H(2s)$	$2\ ^1\Sigma_g$	0.3748003
3	$H(1s) + H(2p)$	$3\ ^1\Sigma_g$	0.3748003
4	$H(1s) + H(3s)$	$4\ ^1\Sigma_g$	0.4442076
5	$H(1s) + H(3p)$	$5\ ^1\Sigma_g$	0.4442076
6	$H(1s) + H(3d)$	$6\ ^1\Sigma_g$	0.4442076
7	$H^-(1s^2) + H^+$	$7\ ^1\Sigma_g$	0.4997332
8	$H(1s) + H(2s)$	$1\ ^1\Sigma_u$	0.3748003
9	$H(1s) + H(2p)$	$2\ ^1\Sigma_u$	0.3748003
10	$H(1s) + H(3s)$	$3\ ^1\Sigma_u$	0.4442076
11	$H(1s) + H(3p)$	$4\ ^1\Sigma_u$	0.4442076
12	$H(1s) + H(3d)$	$5\ ^1\Sigma_u$	0.4442076
13	$H^-(1s^2) + H^+$	$6\ ^1\Sigma_u$	0.4997332

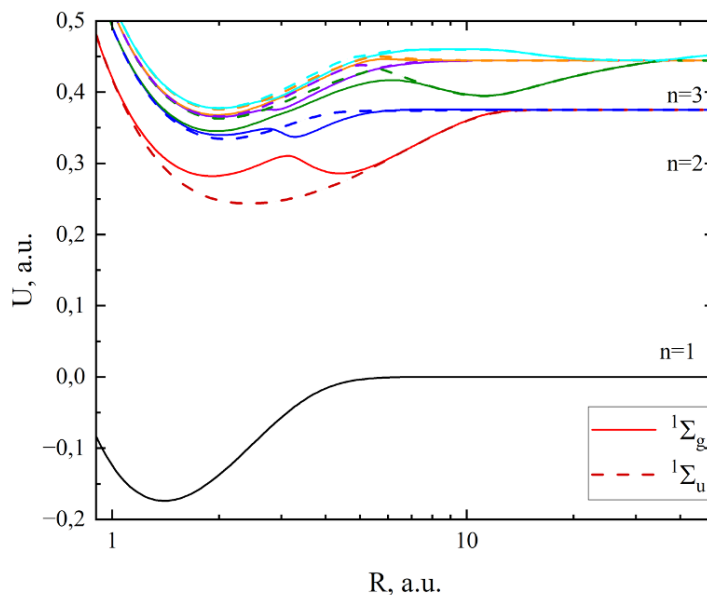


Fig. 1. Adiabatic potentials for H_2 quasimolecule $^1\Sigma_g$ states (solid lines) and $^1\Sigma_u$ states (dashed lines) as functions of internuclear distance

Asymptotic values of radial coupling matrix elements calculated using equation (4) are collected in Table 2. This table shows that besides zero values for transitions between degenerate states, ionic-covalent transitions, and optically forbidden transitions, radial couplings are zero in the asymptotic region for transitions between states of the same parity. However, the calculated radial matrix elements from (Stenrup et al. 2009) have non-zero asymptotic values for couplings between states of the same parity. This artifact may be attributed to the separate calculations for sets of $^1\Sigma_g$ and $^1\Sigma_u$ states.

Table 2. Asymptotic values for $\left\langle j \left| \frac{\partial}{\partial R} \right| k \right\rangle$ matrix elements, terms for molecular states correspond with Table 1

	$1^1\Sigma_g$	$2^1\Sigma_g$	$3^1\Sigma_g$	$4^1\Sigma_g$	$5^1\Sigma_g$	$6^1\Sigma_g$	$7^1\Sigma_g$	$1^1\Sigma_u$	$2^1\Sigma_u$	$3^1\Sigma_u$	$4^1\Sigma_u$	$5^1\Sigma_u$	$6^1\Sigma_u$
$1^1\Sigma_g$	—	0	0	0	0	0	0	0	−0.198	0	−0.094	0	0
$2^1\Sigma_g$	0	—	0	0	0	0	0	0	0	0	−0.061	0	0
$3^1\Sigma_g$	0	0	—	0	0	0	0	0	0	−0.019	0	−0.117	0
$4^1\Sigma_g$	0	0	0	—	0	0	0	0	0.019	0	0	0	0
$5^1\Sigma_g$	0	0	0	0	—	0	0	0.061	0	0	0	0	0
$6^1\Sigma_g$	0	0	0	0	0	—	0	0	0.117	0	0	0	0
$7^1\Sigma_g$	0	0	0	0	0	0	—	0	0	0	0	0	0
$1^1\Sigma_u$	0	0	0	0	−0.061	0	0	—	0	0	0	0	0
$2^1\Sigma_u$	0.198	0	0	−0.019	0	−0.117	0	0	—	0	0	0	0
$3^1\Sigma_u$	0	0	0.019	0	0	0	0	0	0	—	0	0	0
$4^1\Sigma_u$	0.094	0.061	0	0	0	0	0	0	0	0	—	0	0
$5^1\Sigma_u$	0	0	0.117	0	0	0	0	0	0	0	0	—	0
$6^1\Sigma_u$	0	0	0	0	0	0	0	0	0	0	0	0	—

Nuclear dynamics calculations

This work aims to incorporate asymptotic values of radial coupling matrix elements between $1^1\Sigma_g$ and $1^1\Sigma_u$ states, shown in Table 2, into non-adiabatic nuclear dynamics calculations. To include these analytical values of asymptotic radial coupling matrix elements in dynamical calculations, we modify quantum chemical data from (Stenrup et al. 2009) as follows: all radial couplings between states of the same parity are adjusted to reach zero in the asymptotic region; while radial couplings between states of the different parity are set to reach corresponding asymptotic values from Table 2 and have zero values at short and intermediate internuclear distances.

A system of coupled equations (1) is solved for 13 adiabatic states in Table 1 using modified matrix elements for collision energies from 0.001 to 100 eV. Calculated mutual neutralization cross sections are shown with solid lines in Fig. 2: the upper panel shows cross sections for transitions from the $7^1\Sigma_g$ ionic state to all covalent states ($1^1\Sigma_u - 5^1\Sigma_u$ and $1^1\Sigma_g - 6^1\Sigma_g$), and the lower panel — cross sections from the $6^1\Sigma_u$ ionic state. Dashed lines represent independent calculations within each molecular symmetry using initial quantum chemical data. Comparison of these two sets of data shows that cross sections for transitions from both ionic states $7^1\Sigma_g$ and $6^1\Sigma_u$ to the states of the same parity are not sensitive to the change in radial couplings: solid lines almost coincide with dashed lines in both panels of Fig. 2. Meanwhile, cross sections for transitions from each ionic state to the covalent states of different parity have generally much smaller values than to the states of the same parity, with the exception of the $7^1\Sigma_g \rightarrow 1^1\Sigma_g$ transition, which itself has a very small value due to the large energy gap between the $1^1\Sigma_g$ molecular term and other terms (see Fig. 1).

Fig. 3 shows the comparison of mutual neutralization cross sections calculated using the reprojection method and the standard Born–Oppenheimer approach with the upper panel showing transitions from the $7^1\Sigma_g$ state and the lower panel — from the $6^1\Sigma_u$ state; the dashed lines are used for calculations with the reprojection method while the solid lines correspond to calculations based on the standard approach. Cross sections for this figure are summed over final channels $H(1s)+H(nl)$ that have the same quantum number n . It is clearly seen that among mutual neutralization processes the effect of applying the reprojection method is the strongest for transition to the ground state $H(1s)+H(1s)$. These cross sections are in good agreement with the results described in (Stenrup et al. 2009).

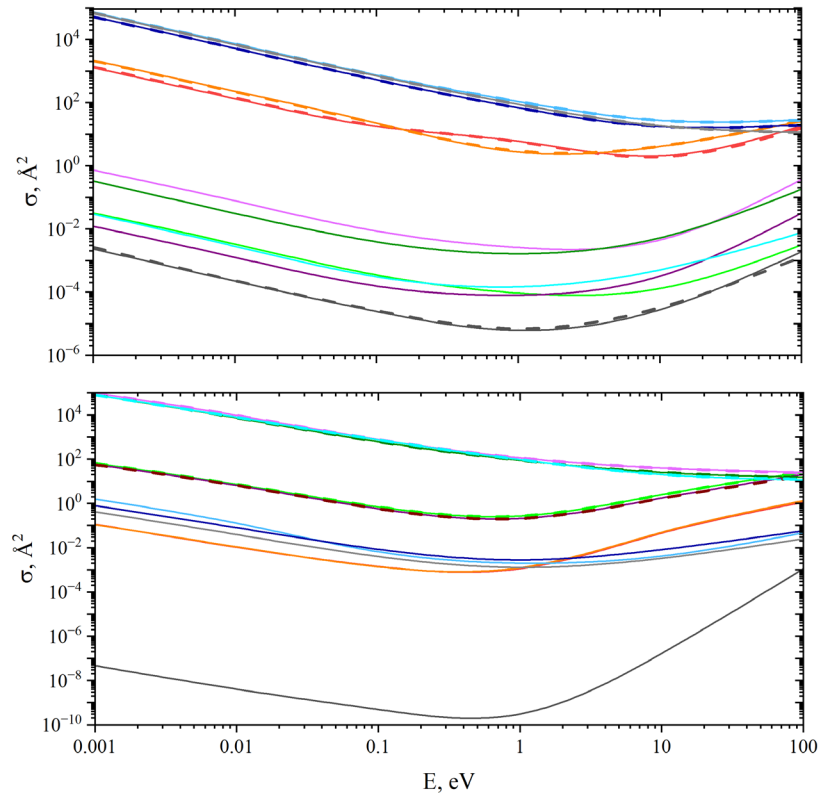


Fig. 2. Partial mutual neutralization cross sections from $7^1\Sigma_g$ state (upper panel) and from $6^1\Sigma_u$ state (lower panel). Solid lines represent calculation in mixed basis of 13 states, while dashed lines stand for calculations within $^1\Sigma_g$ and $^1\Sigma_u$ symmetries separately

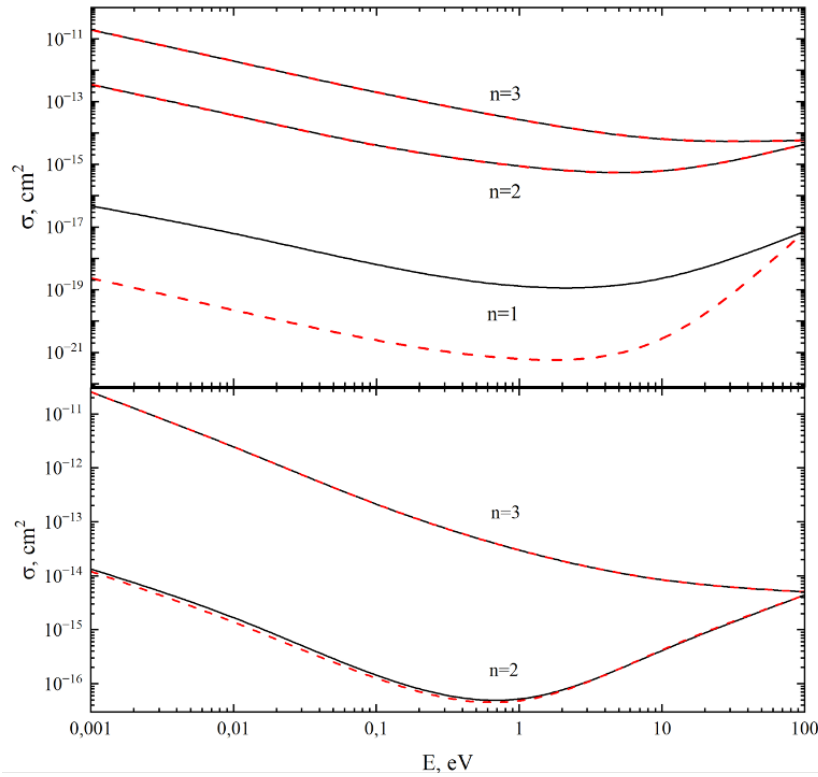


Fig. 3. Mutual neutralization cross sections from the $7^1\Sigma_g$ state (upper panel) and from the $6^1\Sigma_u$ state (lower panel) summed over final channels $H(1s)+H(nl)$ with the same n , calculated within the standard Born–Oppenheimer approach (solid lines) and using the reprojection method (dashed lines)

Conclusion

The mutual neutralization cross sections for $H^- + H^+$ collisions are calculated with the reprojection method that provides correct treatment of non-vanishing radial couplings at large internuclear separations. The basis set for nuclear dynamics consists of seven $^1\Sigma_g$ and six $^1\Sigma_u$ molecular states. Radial matrix elements are adapted for couplings between all 13 states with asymptotic calculated analytically. The analysis of calculated cross sections shows that the presence of asymptotic values couplings between states of different parity slightly redistributes partial mutual neutralization cross sections, though not changing total cross section. However, these asymptotic couplings may have a higher impact on the excitation and de-excitation cross sections.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

Each of the authors contributed to the submission.

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Wind power variations in frequency domain: Introducing a concept of fractional dynamics

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Abstract. We apply a new concept of fractional dynamics in the equation of motion, specifically the harmonic oscillator in non-Euclidean space, to analyze wind speed (WS) in the frequency domain. Frequency spectra (FS) for WS are expressed well by the Mittag-Leffler function (MLF) originating from a concept of *fractional dynamics* in complex systems: FS behaves as $1/f^\alpha$ in high frequencies ($\alpha < 1$). All these findings are compared with those for air temperature (AT), showing $1/f^\alpha$ for WS and $1/f^{2\alpha}$ for AT. An interesting relationship between the $1/f^\alpha$ -law found for WS and $1/f^{2\alpha}$ for AT will be discussed in terms of Newtonian dynamics in the fractional space.

Keywords: wind power, Fast Fourier transform (FFT), fractional relaxation and dynamics, Mittag-Leffler function (MLF), non-Euclidean space, Newtonian dynamics

Introduction

Wind power, one of the major inputs for producing sustainable environmental conditions on the globe (Hasche 2010; Joselin Herbert et al. 2007), is now increasing significantly, while the generated power itself is not stable over time. There are several ways to analyze wind characteristics in the time and/or frequency domain. In the time domain, a simple way is to statistically construct a histogram of the step size (wind speed, etc.) in output over time (Murthy, Rahi 2014; Wan, Bucaneg 2002), and/or variogram time-series analysis has been proposed (Liu et al. 2016). To better understand the nature of *wind quality*, the frequency spectrum (FS) in the frequency domain has been discussed in addition to the time domain, which facilitates the understanding of detailed characteristic features involving periodicity, etc. (Apt 2007).

This paper will identify characteristic features in WS in the frequency domains in three different locations: the Hera campus, Universidade Nacional Timor Lorosa'e, East Timor; the Takayama area (near the mountainside), Gifu, Japan; and the Yanagido campus at Gifu University (Gifu, Japan). We will also discuss ambient temperature (AT) variations in the frequency domains in the same locations.

The WS variations are modeled by the equation of motions, i. e., Newtonian or Lorentz dynamics, as a *fractional* harmonic oscillator, which will be useful in understanding the dynamics in so-called complex systems (Metzler, Klafter 2000). It will be found that the FS behaves as $1/f^\alpha$ for the WS

and $1/f^{2\alpha}$ for the AT ($\alpha < 1$) in high frequencies, while the FS takes a constant in lower frequencies, supporting a significant role of the Mittag-Leffler function introduced in complex systems. An interesting relationship between the $1/f^\alpha$ -law found for WS and $1/f^{2\alpha}$ for AT will also be discussed within a category of Newtonian dynamics.

Measurement system and analysis

First, we discuss WS at the Hera campus, located 10 km east of the Díli city (East Timor) (8.55° S latitude, 125.56° E longitude). The data analyzed in this work were collected from June to September 2019. A 600-watt wind generator set (Nantong R&X Energy Technology: RX-600H3) was utilized. WS was measured at 6-m instrumented towers. The output voltage of the wind turbine was transferred to a data logger (Belo, Shimakawa 2021). Data for WS at every 100 seconds were stored in a PC.

The second example is WS and AT at two stations at the Takayama Field Station, and the third — at the Yanagido campus at Gifu University. The meteorological data observed at the Takayama Field Station of the River Basin Research Center, Gifu University, is used in this study. The Takayama Field Station is located at an elevation of 1.342 m on a high mountainside at 36°8' N latitude and 137°26' E longitude in Gifu, Japan. The observation site is a basin in a complex topography, and the observation instrument is located in an open space of about 1,100 m² surrounded by evergreen coniferous trees of about 20-m height. The wind and temperature sensors are a propeller anemometer (Young 05103-47) and a resistive platinum one (Vaisala HMP-45D), located at a height of 4.23 m and 2.74 m, respectively, from the ground. These data are sampled instantaneously every 10 minutes. The period of the observation data used in this study is 10 years, from January 2008 to December 2017. Another location with the same system is the Yanagido campus, Gifu University (35.4168° N latitude and 136.7769° E longitude). The data are also sampled instantaneously every 10 minutes. The period of the observation data used in this study is 6 years, from January 2017 to December 2022.

All the data of wind speed $v(t)$ are Fourier transformed:

$$v(f) = \int_{-\infty}^{\infty} v(t) e^{-i2\pi ft} dt, \quad (1)$$

where f is the frequency (s⁻¹) and $v(f)$ is the frequency spectrum (FS) (Kogan 2008; Papoulis 1962).

We took the MATLAB program for the Fast Fourier Transform (FFT). When the sampling time is Δt and the data number is given by N , the frequency interval is given as $\Delta f = 1/N\Delta t = 1/t_p$, where t_p is the period of measurement time. The minimum frequency in the FS (by FFT) is therefore $1/t_p$, and the maximum is set to $1/2\Delta t$ (Kogan 2008; Papoulis 1962).

Fractional relaxation and dynamics

Let us begin with the dynamic motion of the particles, with displacement x having a mass of M . It is called the equation of motion, which is the *most fundamental dynamic equation* (Newtonian), given as (Metzler, Klafter 2000)

$$M \frac{d^2 x}{dt^2} + M\Gamma \frac{dx}{dt} + M\omega_0^2 x = F, \quad (2)$$

where Γ is the damping rate, ω_0 is the natural frequency, and F is the external force in Newtonian classical mechanics. A popular example of equation (2) is the so-called harmonic oscillator (HO) (in Euclidean space). The last two terms in equation (2) exhibit the *relaxation* process:

$$M\Gamma \frac{dx}{dt} + M\omega_0^2 x = \frac{dx}{dt} + \frac{x}{\tau} = \frac{F}{M}, \quad (3)$$

where $\omega_0^2/\Gamma \equiv 1/\tau$.

Let us now introduce the concept of fractional dynamics into equation (3). The α -th derivative equation ($0 < \alpha < 1$) is basically used for the fractional relaxation process (in non-Euclidean space) (Belo et al. 2024; Metzler, Klafter 2000).

$$\frac{d^\alpha x}{dt^\alpha} = -\frac{x}{\tau^\alpha}, \quad (4)$$

where F is applied at $t = 0$ and τ^α produces dimensional correctness. The solution of the above equation is given by

$$x(t) = E_\alpha\left(-\left(t/\tau\right)^\alpha\right) = \sum_{k=0}^{\infty} (-1)^k \frac{(t/\tau)^k}{\Gamma(\alpha k + 1)}, \quad (5)$$

which is called the Mittag-Leffler function (Belo et al. 2024; Metzler, Klafter 2000). When $\alpha = 1$, $x(t)$ gives just the exponential function, $\exp(-t/\tau)$. The MLF in the frequency domain is obtained easily by the Laplace transform (LT) of equation (4):

$$s^\alpha x(s) - s^{\alpha-1} x(0) = -\tau^{-\alpha} x(s), \quad (6)$$

where $x(0)$ is the initial value, and s is the Laplace frequency given by $i\omega$. Then we get $x(s)$ as

$$x(s) = \frac{s^{\alpha-1} x(0)}{s^\alpha + \tau^{-\alpha}} = \frac{x(0)}{s(1 + (s\tau)^{-\alpha})}. \quad (7)$$

As $x(s)$ is a position function, the wind speed can be obtained from its derivative. As the MLF is a decay function with t , $v(t)$ is therefore given as $-df(t)/dt$ (Rosa, de Oliveira 2015); the Laplace transform of the above equation gives

$$v(s) = -C(sx(s) - x(0)) = C(1 - sx(s)) = C\left(1 - \frac{s}{s(1 + (s\tau)^{-\alpha})}\right) = \frac{C}{1 + (s\tau)^\alpha}, \quad (8)$$

where C is a constant, $x(0)$ is set to 1, and τ is a relaxation time. Equation (8) is mathematically equivalent to the Cole–Cole relation in dielectrics (solid-state physics) (Cole, Cole 1941), showing a characteristic low-pass filter.

Results and discussion

Fig. 1 shows the measured time-dependent wind speed $v(t)$ at every 100 seconds for three months (8×10^6 s) at the Hera campus (June–September 2019). The maximum wind speed is 35 m/s, and the minimum is 0 m/s, with roughly 1-day periodicity (diurnal), which is a general trend in wind power reported in other areas (Apt 2007).

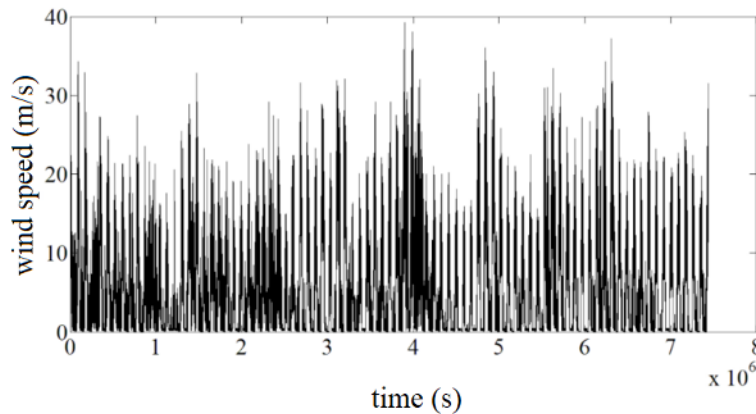


Fig. 1. Time-variation of the wind speed $v(t)$ at every 100 seconds for three months (8×10^6 s) at the Hera campus (June–September 2019)

Let us discuss the wind speed variation in the frequency domain. Fig. 2 shows the frequency spectrum (FS: black solid line), $|v(f)|$, directly calculated from the FFT of $v(t)$, together with a model prediction (red solid line) given by equation (8), with $C = 0.50$, $\alpha = 0.50$, and $\tau = 1.0 \times 10^5$ s. At around 10^{-5} Hz,

a peak is observed, which corresponds to a 1-day period. The 2nd harmonicity (peak) appears at a half-day cycle. Fitting equation (8) to practical data is reasonably good.

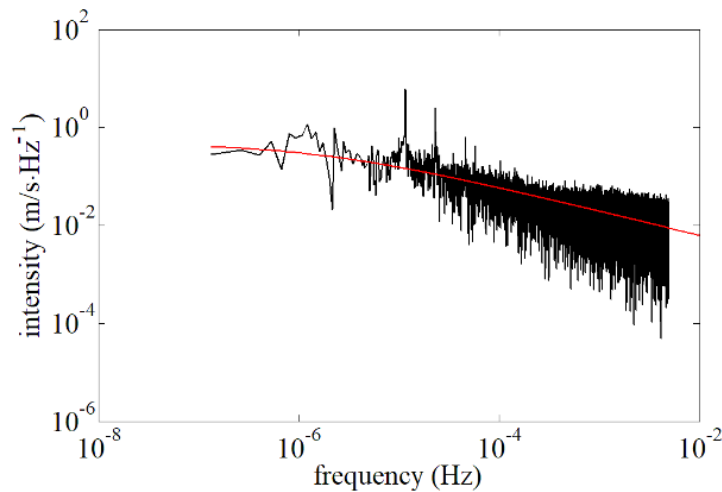


Fig. 2. Frequency spectrum $|\nu(f)|$ of wind speed at the Hera campus. The solid line is predicted from equation (8), with $C = 0.50$, $\alpha = 0.50$, and $\tau = 1.0 \times 10^5$ s ($R^2 = 0.41$)

Let us discuss the WS variation in other locations. Fig. 3 shows the measured time-dependent WS at every 600 seconds for 10 years (from January 2008 to December 2017: about 3.2×10^8 s) at the Takayama Field Station. The maximum WS is 5 m/s, which is observed around August, and the minimum is around 0 m/s. The maximum wind speed is small because strong wind is shaded by the complex topography and tall trees around the observation site. The WS time series shows the periodicity in a one-year period (Climate change monitoring report 2015).

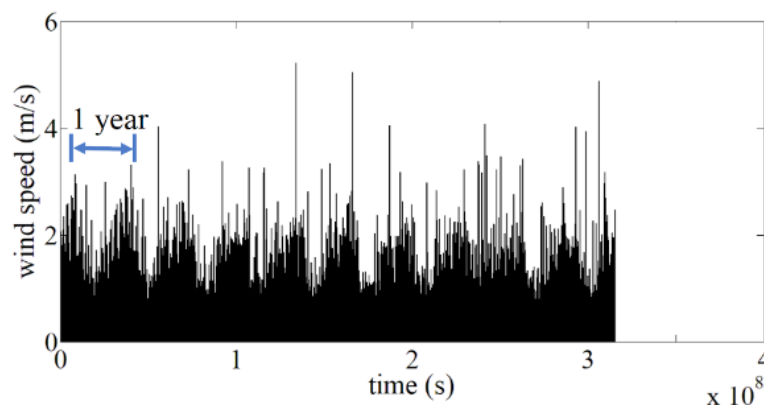


Fig. 3. Time domains of wind speed from January 2008 to December 2017 at Takayama

Fig. 4 shows the FS for the WS. The FS shows the principal peaks around 1 year and 1 day. Around a 1-year peak, it takes a constant value and decreases with increasing frequency. The solid (red) line shows the applicability of fractional dynamics prediction from equation (8) with $C = 0.01$, $\alpha = 0.60$, and $\tau = 2 \times 10^5$ s for the WS with $R^2 = 0.46$.

Fig. 5 shows the measured time-dependent WS at every 600 seconds for 6 years (from January 2017 to December 2022: about 2.1×10^8 s) at Yanagido as the last example. The maximum WS is ~ 20 m/s, observed in or around August.

Fig. 6 shows the FS for the WS, estimated from the raw time-dependent data indicated in Fig. 5. Overall features are almost the same as those in Fig. 4. The solid (red) line in (a) denotes the applicability of fractional dynamics prediction from equation (8) with $C = 0.07$, $\alpha = 0.6$, and $\tau = 2.0 \times 10^5$ s for the WS with $R^2 = 0.53$, in which α is also a bit larger than that ($= 0.50$) of the Hera campus (see Fig. (2)).

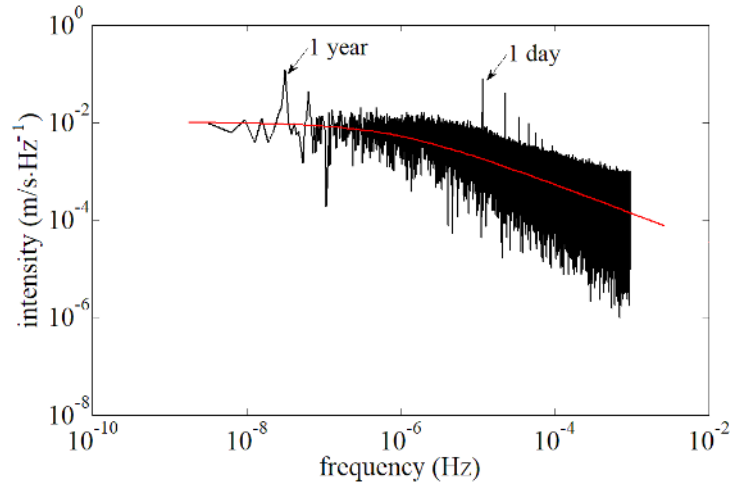


Fig. 4. Frequency spectrum $|F(f)|$ of WS at Takayama for 2008 to 2017, together with the model prediction (red solid line), with $C = 0.01$, $\alpha = 0.60$, and $\tau = 2.0 \times 10^5$ s ($R^2 = 0.46$)

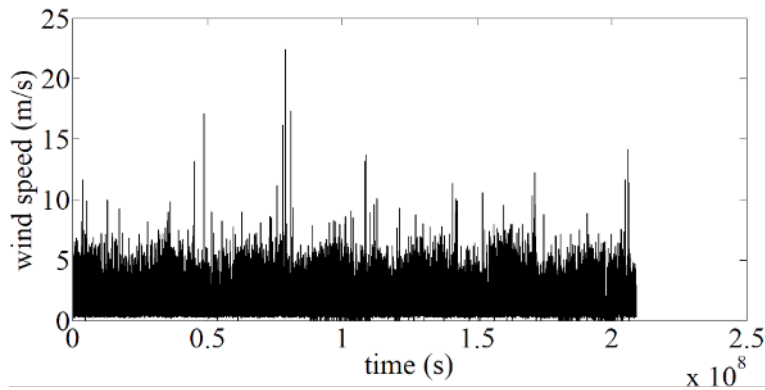


Fig. 5. Time domains of wind speed from January 2017 to December 2022 at Yanagido (Gifu)

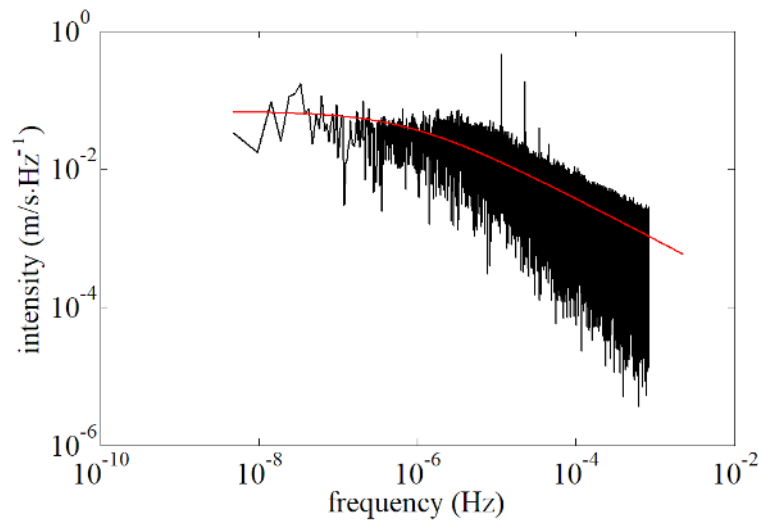


Fig. 6. Frequency spectrum $|F(f)|$ of WS at Yanagido for January 2017 to December 2022, together with the model prediction (red solid line), with $C = 0.07$, $\alpha = 0.60$, and $\tau = 2.0 \times 10^5$ s ($R^2 = 0.53$)

Fig. 7 presents the atmospheric (air) temperature variations measured at Takayama (a) and the Yanagido campus, Gifu University (b). The data were collected every 600 seconds for 10 years ($\sim 3.2 \times 10^8$ s) from January 2008 to December 2017 at Takayama and for 6 years ($\sim 2.1 \times 10^8$ s) from January 2017 to December 2022 at the Yanagido campus. The maximum AT is 34°C and 38°C ($\sim$ in August), and the minimum is -15°C and -5°C ($\sim$ in February), respectively. It means that AT at Takayama is much colder than that at the Yanagido campus. The AT time series shows the periodicity in one year for both. In wintertime (December–January–February), northwesterly winds cause the advection of cold air from Siberia to Japan, bringing heavy snowfall to Japan's Sea of Japan side. At this time the temperature tends to be low (Japan Meteorological Agency 2015). In summertime (June–July–August), in the second half of summer, the North Pacific High extends northwestwards around Japan, bringing hot and sunny conditions to the country. At this time the temperature tends to be high, causing cool and moist easterly winds (Japan Meteorological Agency 2015).

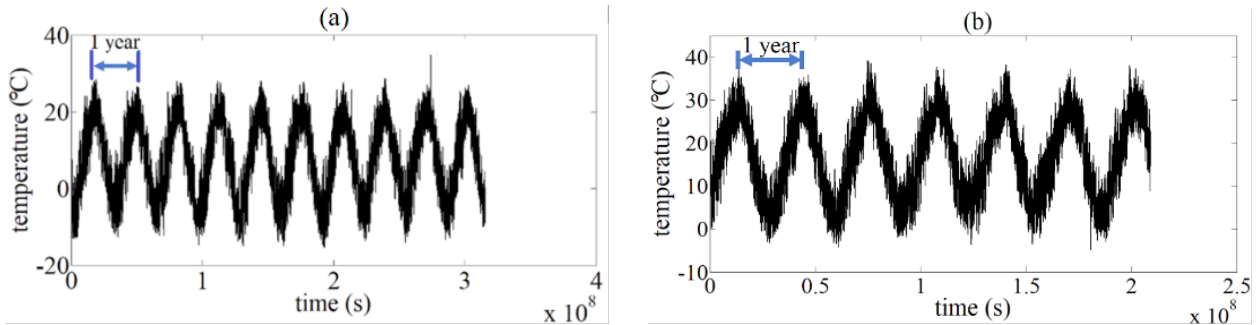


Fig. 7. Time domain AT (a) from January 2008 to December 2017 at Takayama and (b) from January 2017 to December 2022 at Yanagido (Gifu)

Fig. 8 shows frequency spectrum (FS) for the AT at (a) Takayama and (b) the Yanagido campus. FS shows the principal peaks around 1 year and 1 day. Around a 1-year peak, it takes a constant value and decreases with increasing frequency, which is the same behavior as the $|F(f)|$ of WS (see Figs. 4 and 7). We therefore try to use the same equation as equation (8). Note, however, that a constant B is used for AT instead of C in equation (8). The solid (red) line in (a) shows the prediction from equation (8) with $\alpha = 1.1$, $\tau = 2 \times 10^5$ s, and $B = 0.20$ ($R^2 = 0.56$), and in (b) we get $\alpha = 1.1$, $\tau = 2 \times 10^5$ s, and $B = 0.22$ ($R^2 = 0.58$). Note that the α -values for AT are almost twice those of WS, while τ is kept the same. As the kinetic energy of wind should be proportional to the squared wind speed v^2 , $T(f)$ is therefore proportional to $|v(f)|^2$. This is why the α -value for AT shows roughly twice that for WS.

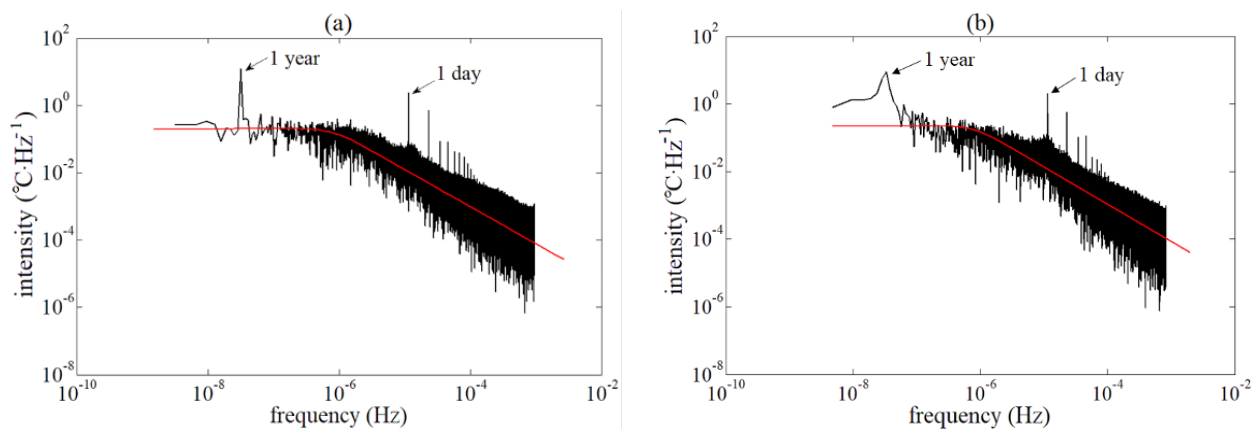


Fig. 8. Frequency spectrum $|T(f)|$ of air temperature at (a) Takayama for 2008 to 2017 and (b) Yanagido for January 2017 to December 2022. The solid line is given from equation (8), with $\alpha = 1.10$, $\tau = 2 \times 10^5$ s, and $B = 0.20$ ($R^2 = 0.56$) (a), and with $\alpha = 1.10$, $\tau = 2 \times 10^5$ s, and $B = 0.22$ ($R^2 = 0.58$) (b), respectively.

Conclusion

The variation of the wind speed and air temperature through time- and frequency-domains at different locations in East Timor and Japan was discussed by introducing a new concept of fractional dynamics. It was found that the frequency of wind speed (frequency histogram) is approximately given by the well-known Weibull distribution in all locations. We found that the dynamic change for WS is replicated well by the Mittag-Leffler function, originating from a concept of the *fractional dynamics* in complex systems. The FS behaves as $1/f^\alpha$ for the WS and $1/f^{2\alpha}$ for the AT in the high-frequency range ($\alpha < 1$). An interesting correlation between WS and AT was discussed in terms of Newtonian dynamics.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All authors made an equivalent contribution to the preparation of the publication.

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Wind power variations in time domain: Introducing a waiting time probabilistic distribution

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Abstract. Time-dependent changes in wind speed (WS) observed at different locations in East Timor and Japan are analyzed using a statistical approach in the time domain. The WS histogram is approximated to be the Weibull distribution at two different locations. The reason why the histogram follows the Weibull distribution will be discussed through a generalization of the Rayleigh distribution which has been originally applied to the scattering of the electromagnetic wave. It is also found that the waiting time probability density for WS, defined as the time spent by the wind speed below or above a given threshold value, is presented by a power-law scaling with time as $t^{-\alpha}$ ($\alpha < 2.5$), which will be associated with long-term correlations, but not a Poisson-type distribution. A new concept of fractional dynamics within the stochastic analysis of WS will be presented.

Keywords: wind power, stochastic approach, waiting time distribution, Weibull distribution, fractional dynamics

Introduction

Wind power should be a major energy source for maintaining sustainable environmental conditions on the globe (Hasche 2010; Joselin et al. 2007). However, wind power is inherently unstable, and the power produced by turbines fluctuates significantly over time. Therefore, it is necessary to understand the characteristic features of these variations through the establishment of standard analytical techniques, regardless of location. There are two primary approaches to analyzing wind characteristics, namely analyses in the time and the frequency domains (Apt 2007; Bucaneg, Wan 2002; Liu et al. 2016; Murthy, Rahi 2014).

In the time domain, a simple way is to construct a statistical histogram of the wind speed (Bucaneg, Wan 2002; Murthy, Rahi 2014) and to apply variogram time-series analysis (Liu et al. 2016). It is well known that the wind speed histogram follows the Weibull distribution (Matsfelt, Davidson 2018; Murthy, Rahi 2014). In the frequency domain, the frequency spectrum (FS) helps to elucidate detailed features associated with periodicity (Apt 2007).

In the present study, we investigate WS in the time domain at two different locations: near the seaside in East Timor and on the mountain side in Japan. At both locations, the wind speed histogram is well approximated by the Weibull distribution. The reason why the histogram follows the Weibull distribution is discussed in terms of a generalization of the Rayleigh distribution which has been originally applied to the scattering of the electromagnetic wave (Hofmann, Okafor 2001; Muller et al. 2002). We further examine the waiting time statistics, defined as the time during which the wind speed remains below or above a given threshold value. To our knowledge, the waiting time distribution $\Psi(t)$ for wind speed has not yet been fully understood. We find that $\Psi(t)$ follows a power-law scaling with time as $t^{-\alpha}$ ($\alpha < 2.5$), indicating the presence of long-term correlations rather than a correlated Poisson-type distribution.

Experimental

We measured wind speed (WS) variations in the time domain at two different locations. One site was the Hera campus, located 10 km east of the Díli city, East Timor (8.55° S latitude, 125.56° E longitude), where measurements were conducted from June to September 2019. Wind speed was measured using a 6-m instrumented tower equipped with a 600 W wind generator (Nantong R&X Energy Technology: RX-600H3). The output voltage of the wind turbine was recorded every 100 s by a data logger, yielding a total of $N_T = 74398$ (Belo, Shimakawa 2021).

The second WS dataset was obtained at the Takayama Field Station of the River Basin Research Center, Gifu University. The station is located on a high mountainside at an elevation of 1,342 m at 36°8' N latitude and 137°26' E longitude in Gifu, Japan. The observation site lies within a basin characterized by a complex topography, and the instrument is installed in an open area of approximately 1,100 m², surrounded by evergreen coniferous trees about 20 m in height. Wind speed was measured using a propeller anemometer (Young 05103-47) mounted at a height of 4.2 m. The data were sampled every 10 mins from January 2008 to December 2017 (for 10 years), yielding a total of $N_T = 525,600$ data points.

Results

Fig. 1 shows the time variation of the wind speed $v(t)$, measured every 100 s over three months (June — September 2019) at the Hera campus. Before proceeding to the discussion of our main focus area, i. e., the waiting-time statistics of wind speed, to get overall features of wind power, we first discuss the histogram for the wind speed $v(t)$ in which the probability density at a particular wind speed is obtained. The number of occurrences of each speed N is counted for this project.

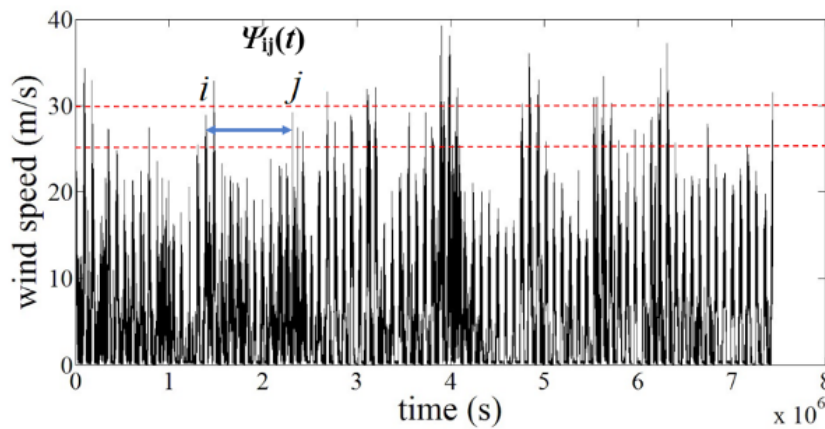


Fig. 1. Time-variation of the wind speed $v(t)$, measured every 100 s over three months at the Hera campus. Waiting time t_{ij} is defined as the time interval between the i -th and j -th events within a selected velocity range, for example, $25 \leq v < 30$ (red dashed lines)

Discrete bars shown in Fig. 2 represent the normalized wind speed distribution, N/N_T , where $N_T = 74,398$ is the total number of data points. It is well known that the Weibull distribution is widely accepted and commonly used for wind data analysis (Matsfelt, Davidson 2018; Murthy, Rahi 2014).

We therefore examine whether the wind speed follows the Weibull distribution, as shown by the solid red line and given as

$$W(v) = A \frac{k}{c} \left(\frac{v}{c}\right)^{k-1} \exp\left[-\left(\frac{v}{c}\right)^k\right], \quad (1)$$

where k is the shape parameter, c is the scale parameter (with the same units as wind speed, ms^{-1}), and A is the fitting parameter.

The solid line in Fig. 2 represents the probability density $W(v)$ (equation (1)), obtained using the parameters $A = 1.35$, $c = 11.5$, and $k = 2.1$. This model reproduces the experimental observation reasonably well ($R^2 = 0.82$), although the histogram itself shows some scatters. Note that the well-known Rayleigh distribution corresponds to the special case, $k = 2.0$ (Hofmann, Okafor 2001; Muller et al. 2002).

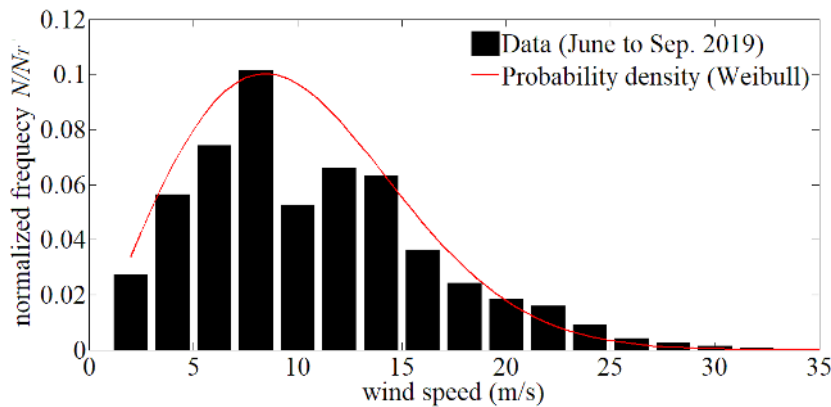


Fig. 2. Normalized wind speed distribution (histogram) and the Weibull distribution at the Hera campus with fitting parameters ($A = 1.35$, $c = 11.5$, $k = 2.1$) ($R^2 = 0.82$)

Let us now discuss how to define the waiting time distribution (WTD) for a particular wind speed, as shown in Fig. 1. From the waiting time t_{ij} , i. e., the time interval between the i -th and j -th events within a selected velocity range between v and $v + dv$, the waiting time probability density $\Psi_{ij}(t)$ between the i -th and j -th events can be deduced from the number of occurrences N_v (histogram) divided by the total number of events (N_{vT}) in a manner similar to the wind speed distribution (see Fig. 2). In the following, we present the experimentally obtained $\Psi(t)$ (normalized event number), discussing their scientific insight in Section IV.

Fig. 3 shows the *normalized* histogram (dots) of waiting time, i. e., N_v/N_{vT} , which is defined as the waiting time probability density $\Psi(t)$ (s^{-1}) (solid line), for $v < 5$ (a), $5 \leq v < 10$ (b), $10 \leq v < 15$ (c), $15 \leq v < 20$ (d), $20 \leq v < 25$ (e), and $v \geq 25$ (f). $\Psi(t)$ is approximately given by a power law as

$$\Psi(t) = C t^{-\alpha}, \quad (2)$$

where C is a constant, t is time (s), and α is a numerical parameter. The fitting parameters are listed in Table 1. It is found that the value of α is approximately 2, except for $v \geq 25$ m/s. The reason why $\Psi(t)$ follows a power law will be discussed in Section IV.

Let us now discuss WS in another place (Takayama, Japan). Fig. 4 shows the WS histogram (a) for the period 2008–2017 (10 years), with a total number of data points $N_T = 526,027$, obtained in the same manner as in Fig. 2 (Hera campus), and (b) for 2017 (1 year), with a total number of data points $N_T = 52,560$. There is no significant difference between (a) and (b) in Fig. 4, suggesting that climate change found globally cannot be affected for the Weibull parameters A , c , and k (see figure caption) between 2017 and the period of 2008–2017.

Let us now turn to the waiting time probability density $\Psi(t)$ (s^{-1}). Fig. 5 shows the waiting time histogram (dots) and the waiting time probability density $\Psi(t)$ (s^{-1}) (solid line for fitting) at Takayama (Japan): (a) for $v < 0.25$, (b) for $0.25 \leq v < 0.5$, (c) for $0.5 \leq v < 1.0$ and (d) $v \geq 1.0$. Similar to the Hera campus results, $\Psi(t)$ (s^{-1}) is also well approximated by a power law (see equation (3)). The fitting parameters for Fig. 5 are listed in Table 2.

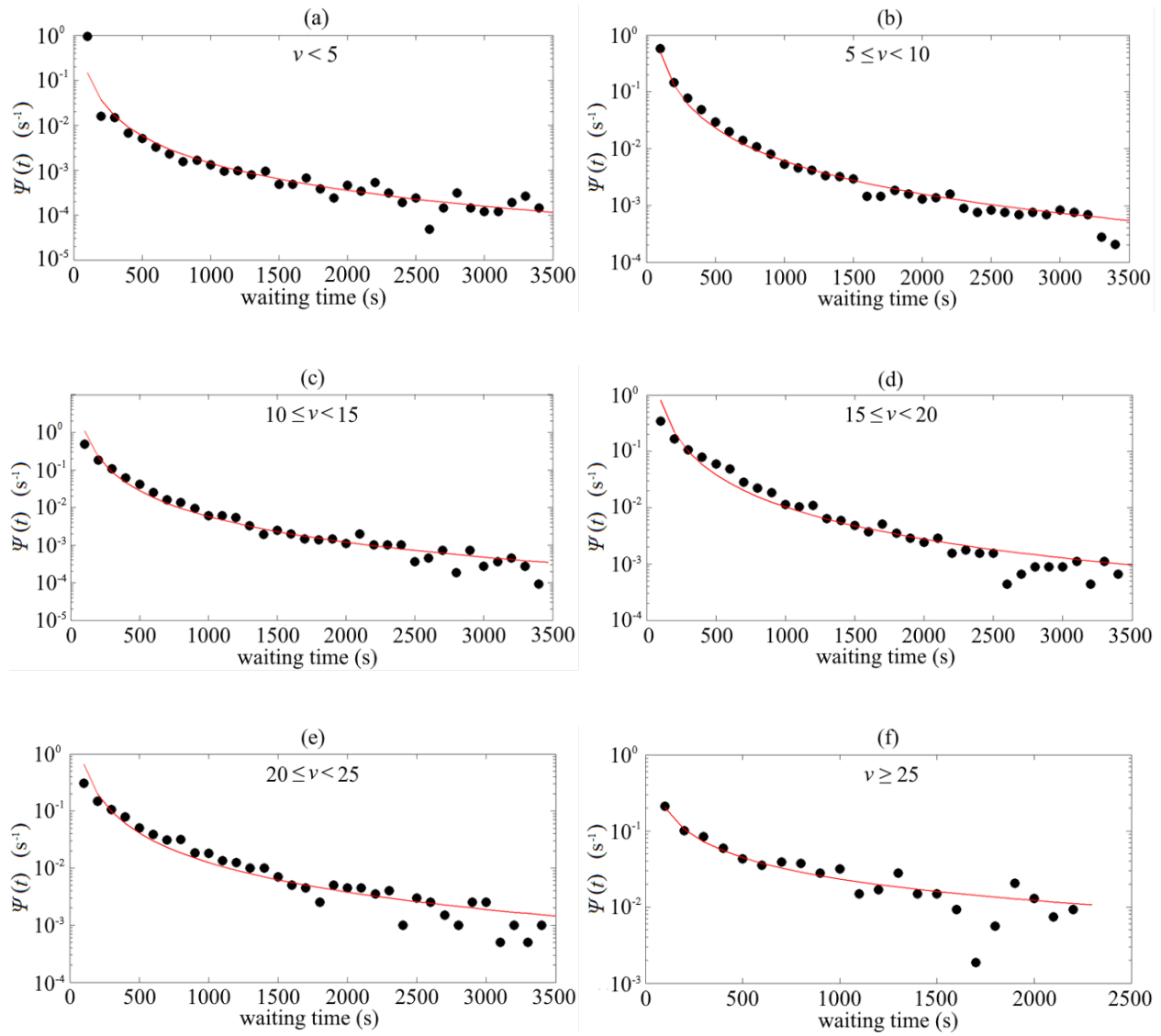


Fig. 3. Waiting time probability density for $\nu < 5$ (a), $5 \leq \nu < 10$ (b), $10 \leq \nu < 15$ (c), $15 \leq \nu < 20$ (d), $20 \leq \nu < 25$ (e), and $\nu \geq 25$ (f)

Table 1. Fitting parameters for the power law (see equation (2))

	C	α	R^2
(a)	1.5×10^3	2.0	0.940
(b)	3.6×10^3	1.9	0.999
(c)	3.7×10^4	2.3	0.954
(d)	5.0×10^3	1.9	0.910
(e)	1.8×10^3	1.7	0.904
(f)	1.5×10^1	0.94	0.577

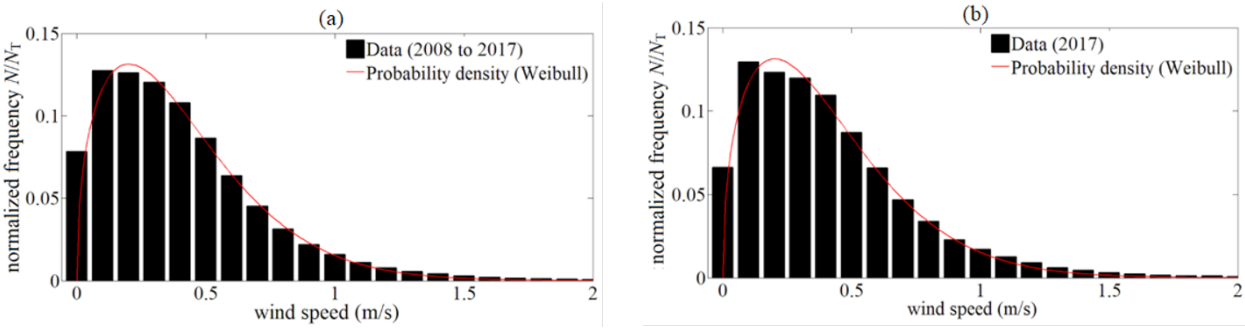


Fig. 4. Histogram of wind speed for (a) the 2008–2017 period at Takayama: $W(v)$ (solid line) fitted with $A = 0.08$, $c = 0.45$, and $k = 1.45$ ($R^2 = 0.86$), and for (b) January–December 2017: $W(v)$ (solid line) fitted with $A = 0.08$, $c = 0.45$, and $k = 1.45$ ($R^2 = 0.89$)

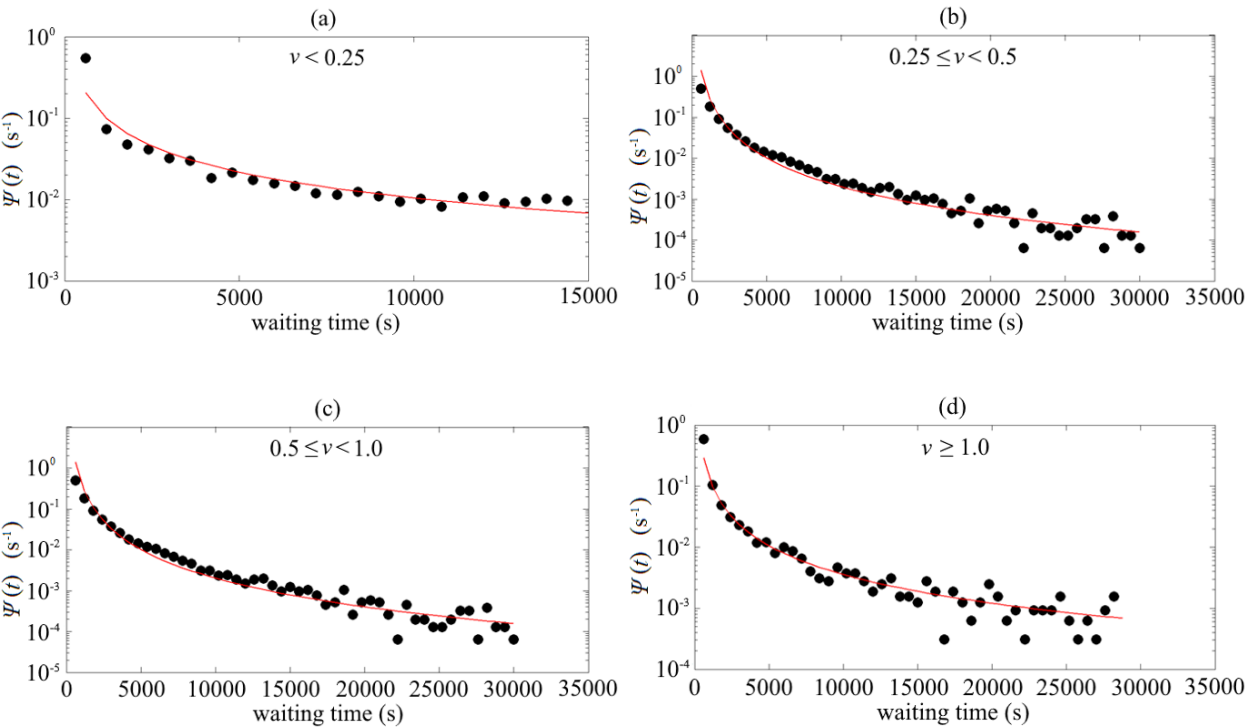


Fig. 5. Waiting time probability density for $v < 0.25$ (a), $0.25 \leq v < 0.5$ (b), $0.5 \leq v < 1.0$ (c), $v \geq 1.0$ (d)

Table 2. Fitting parameters for the power law (see equation (2))

	C	α	R^2
(a)	1.8×10^2	1.1	0.863
(b)	4.0×10^6	2.3	0.961
(c)	4.7×10^4	1.8	0.998
(d)	6.4×10^3	1.6	0.953

Discussion

The previous section showed that the histogram of the wind speed variation over a given period is described by the Weibull-type probabilistic distribution $W(v)$ (see Fig. 2 and 4). It was also shown that the waiting-time distribution $\Psi(t)$ for producing a wind speed v follows a power law (equation (2)).

In the present section, we first discuss the origin of $W(v)$ used in the wind speed v (equation (1)). An easier approach may be a generalization of the Rayleigh distribution (RD), i. e., the case $k = 2$ in equation (1) (Hofmann, Okafor 2001; Muller et al. 2002), where the RD is regarded as a special case of the Weibull distribution. Note that the RD was originally applied to propagating electromagnetic waves with random reflection and scattering (a two-dimensional random vector), although wind (or sound) waves are completely different from electromagnetic waves. In the RD, the magnitude of the signal intensity A is given by

$$P_{RD}(A) = 1 - \exp\left[-\left(\frac{A}{c}\right)^2\right], \quad (3)$$

where the variable A is used for the RD, but not velocity v . The probability density, $dP_{RD}(A)/dA$, is then given by

$$dP_{RD}(A)/dA = \frac{2}{c}\left(\frac{A}{c}\right) \exp\left[-\left(\frac{A}{c}\right)^2\right]. \quad (4)$$

Note that equation (4) is equivalent to equation (1) with $k = 2$. The exponent k , when smaller than 2, can be predicted from the concept of fractional dynamics. A vector representation in fractional space can be introduced: e. g., $x^2 + y^2 = r^2$ is transferred into $x^\alpha + y^\beta = r^\gamma$ (non-integer $\alpha, \beta, \gamma < 2$). Consequently, $k = 2$ in Euclid space can be modified to $k < 2$ in non-Euclid space (Vicsek 1989).

Next, we will discuss the waiting-time distribution $\Psi(t)$. We begin with the well-known Poisson waiting time distribution in the time domain given as (Papoulis 1965)

$$\Psi(t) = \lambda \exp(-\lambda t), \quad (5)$$

where λ is a constant with dimension s^{-1} . We further assume that wind can be generated by a pressure (potential) difference between two blocked random sites (i. e., a potential barrier U), as shown in Fig. 6. The parameter λ can be determined by a potential energy barrier U and is given by

$$\lambda = \lambda_0 e^{-\frac{U}{U_0}}, \quad (6)$$

where λ_0 and U_0 are constants.

In complex processes, such as wind scattering, the potential U may have distribution, e. g.,

$$P(U) = \frac{1}{U_m} e^{-\frac{U}{U_m}}, \quad (7)$$

where U_m is a constant. Then, λ is distributed in some manner $G(\lambda)$ given by (Papoulis 1965)

$$G(\lambda) = \frac{P(U)}{\left|\frac{d\lambda}{dU}\right|} = \frac{U_0}{\lambda} \frac{1}{U_m} e^{-\frac{U}{U_m}} = \frac{U_0}{\lambda} \frac{1}{U_m} e^{\frac{U_0 \ln(\lambda/\lambda_0)}{U_m}} = \frac{k}{\lambda} \left(\frac{\lambda}{\lambda_0}\right)^k \propto \lambda^{k-1}, \quad (8)$$

where $k = U_0/U_m$. Equation (5) is then modified to

$$\Psi(t) = \int G(\lambda) \lambda \exp(-\lambda t) d\lambda = C \int \lambda^k e^{-\lambda t} d\lambda = C t^{-1-k} = C t^{-\alpha}, \quad (9)$$

where C is a constant and $\alpha = 1 + k$, replicating well the experimental data (see Fig. 3 and 5). The parameter k may depend on the wind speed v , since complexities such as wind scattering etc. should be different for v .

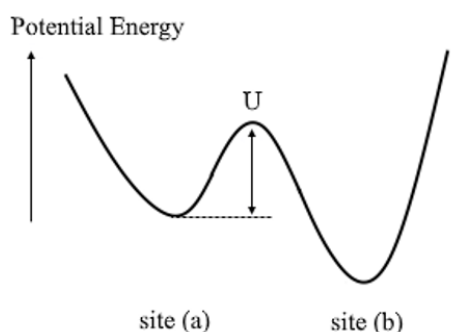


Fig. 6. Potential barrier U between two sites (a) and (b)

Conclusions

Time variations in wind speed at different locations, near the seaside in East Timor and on the mountain side in Japan, were analyzed using a statistical approach in the time domain. The WS histograms at these locations were well approximated by the Weibull distribution. The reason for following the Weibull distribution was discussed in terms of the generalization of the Rayleigh distribution. The waiting time probability density for WS, defined as the time during which the wind speed remains below or above a given threshold value, was found to follow a power law scaling with time, $t^{-\alpha}$ ($\alpha < 2.5$). This behavior may be associated with long-term correlations and is not consistent with a Poisson-type distribution. It was found that the characteristic features of $W(v)$ and $\Psi(t)$ were almost the same even at completely different locations on our globe.

Conflict of Interest

The authors declare that there is no conflict of interest, either existing or potential.

Author Contributions

All authors made an equivalent contribution to the preparation of the publication.

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Физика конденсированного состояния

ВЛИЯНИЕ УРОВНЯ КОНЦЕНТРАЦИИ СЕНСИБИЛИЗИРУЮЩИХ КРАСИТЕЛЕЙ НА ФОТОВОЛЬТАИЧЕСКИЙ ЭФФЕКТ В МОНОКРИСТАЛЛИЧЕСКОМ КРЕМНИИ N-ТИПА В ОПТИЧЕСКОМ ДИАПАЗОНЕ

Михаил Александрович Горяев, Александр Павлович Смирнов

Аннотация. Исследовано влияние органических красителей, находящихся на поверхности монокристаллического кремния n-типа, на проявление фотовольтаического эффекта. Изучены особенности сенсibilизированного фотовольтаического эффекта в случае использования красителей эритрозина и метиленового голубого в роли сенсibilизаторов при различных концентрациях. Итоговые результаты обсуждаются с точки зрения механизма безызлучательного индуктивно-резонансного переноса поглощаемой красителем энергии на поверхность кристалла кремния.

Ключевые слова: монокристалл кремния n-типа, эритрозин и метиленовый голубой, сенсibilизированный фотовольтаический эффект, концентрация сенсibilизаторов, спектры поглощения сенсibilизаторов.

Для цитирования: Goryaev, M. A., Smirnov, A. P. (2026) Influence of the concentration value of sensitizing dyes on the photovoltaic effect in monocrystalline n-type silicon in the optical region. *Physics of Complex Systems*, 7 (3), 106–110. <https://www.doi.org/10.33910/2687-153X-2026-7-3-106-110> EDN [TNBLEU](#)

АНАЛИТИЧЕСКИЕ РЕШЕНИЯ УРАВНЕНИЙ ДВУХФАЗНОЙ ОБЛАСТИ ПРИ НАЛИЧИИ НАБЕГАЮЩЕГО ПОТОКА

Ирина Евгеньевна Корозникова

Аннотация. В работе описывается процесс направленной кристаллизации. Учтено наличие двухфазной области, а также слабое исходящее или входящее течение в ней. Математическая модель составлена с учетом этих дополнений. Решение было получено полностью аналитически. В работе определены концентрации примеси в зависимости от доли твердой фазы, температуры, доли твердой фазы, толщина двухфазной области. Также было получено междендритное расстояние от скорости кристаллизации и течения с помощью критерия отбора. Были построены зависимости концентрации от доли твердой фазы в сравнении с экспериментальными данными, проницаемость двухфазной области от координаты, а также междендритное расстояние от скорости кристаллизации в сравнении с экспериментальными данными. Во всех случаях полученная теория имеет прекрасное согласование с экспериментальными данными.

Ключевые слова: направленное затвердевание, двухфазная область, слабое течение, тепло-массоперенос, точные аналитические решения, нелинейные системы уравнений.

Для цитирования: Koroznikova, I. E. (2026) Analytical solutions of two-phase region equations in the presence of an incoming flow. *Physics of Complex Systems*, 7 (3), 111–122. <https://www.doi.org/10.33910/2687-153X-2026-7-3-111-122> EDN [OVNYLU](#)

Теоретическая физика

ЗА ПРЕДЕЛАМИ СТАНДАРТНОГО КВАНТОВОГО ЭФФЕКТА ЗЕНОНА

Андрей Александрович Борисов, Антон Александрович Борисов, Тимур Фянович Камалов

Аннотация. В настоящей работе введен функционал скорости декогеренции квантовой системы. Квантовая система представляет собой кубит, который может находиться в состоянии $|1\rangle$, $|0\rangle$ или в суперпозиции. Помимо внешней дефазировки и зеноновской скорости затухания, действующих на квантовую систему, учитываются ресурсные потери измерительного канала. Показано, что при параметрах задачи, соответствующих пределу идеально частых измерений в квантовом эффекте Зенона, устойчивость состояния кубита не повышается. Установлено существование

оптимального значения интервала времени и параметра неидеальности измерения, при которых достигается минимум скорости декогеренции состояния кубита. Расчеты показывают, что в рассматриваемом случае время когерентности кубита увеличивается в 11,5 раза, что обеспечивает повышение устойчивости состояния кубита.

Ключевые слова: устойчивость, кубит, квантовый эффект Зенона, минимум, неидеальность измерения, принцип устойчивости.

Для цитирования: Borisov, A. A., Borisov, A. A., Kamalov, T. F. (2026) Beyond the standard quantum Zeno effect. *Physics of Complex Systems*, 7 (3), 123–130. <https://www.doi.org/10.33910/2687-153X-2026-7-3-123-130> EDN RFNHQO

УЧЕТ АСИМПТОТИЧЕСКИХ ЗНАЧЕНИЙ НЕАДИАБАТИЧЕСКИХ СВЯЗЕЙ В ИССЛЕДОВАНИИ ДИНАМИКИ КВАЗИМОЛЕКУЛЫ H_2

Светлана Анатольевна Яковлева, Татьяна Сергеевна Малеева, Максим Юрьевич Яковлев

Аннотация. В работе исследованы процессы взаимной нейтрализации при столкновениях $H^- + H^+$ с помощью метода перепроецирования в рамках подхода Борна — Оппенгеймера. Данный метод позволяет проводить расчеты ядерной динамики с использованием радиальных матричных элементов неадиабатичности, не обращающихся в ноль при больших межъядерных расстояниях. Расчеты ядерной динамики проведены для смешанного базиса молекулярных состояний $^1\Sigma_g$ и $^1\Sigma_u$, а радиальные матричные элементы выведены на асимптотические значения, рассчитанные аналитически. Сечения парциальных процессов взаимной нейтрализации рассчитаны для энергий столкновения от 0,001 до 100 эВ.

Ключевые слова: неупругие процессы, неадиабатические переходы, асимптотические матричные элементы, взаимная нейтрализация, сечения, водород.

Для цитирования: Yakovleva, S. A., Maleeva, T. S., Yakovlev, M. Yu. (2026) Account of asymptotic couplings in collisional dynamics of H_2 quasimolecule. *Physics of Complex Systems*, 7 (3), 131–136. <https://www.doi.org/10.33910/2687-153X-2026-7-3-131-136> EDN YHMEJH

КОЛЕБАНИЯ СИЛЫ ВЕТРА В ЧАСТОТНОЙ ОБЛАСТИ: ПРИМЕНЕНИЕ ПОНЯТИЯ ДРОБНОЙ ДИНАМИКИ

Абелито Филипе Бело, Коити Симакава

Аннотация. Новая концепция дробной динамики при рассмотрении уравнений движения, в частности, при рассмотрении движения гармонического осциллятора в неевклидовом пространстве, применена для анализа частотной зависимости силы ветра (СВ). Частотный спектр (ЧС) для СВ хорошо описывается функцией Миттаг-Леффлера (ФМЛ), взятой из концепции дробной динамики: ЧС ведет себя как $1/f^\alpha$ в области высоких частот ($\alpha < 1$). Сравнение полученных результатов с данными по температуре воздуха (ТВ) показало зависимость $1/f^\alpha$ для СВ и $1/f^{2\alpha}$ для ТВ. Интересная взаимосвязь между законом $1/f^\alpha$ для СВ и $1/f^{2\alpha}$ для ТВ рассмотрена с точки зрения ньютоновской динамики в дробном пространстве.

Ключевые слова: сила ветра, быстрое преобразование Фурье (БПФ), дробная релаксация и динамика, функция Миттаг-Леффлера (ФМЛ), неевклидово пространство, ньютоновская динамика.

Для цитирования: Belo, A. F., Shimakawa, K. (2026) Wind power variations in frequency domain: Introducing a concept of fractional dynamics. *Physics of Complex Systems*, 7 (3), 137–143. <https://www.doi.org/10.33910/2687-153X-2026-7-3-137-143> EDN XKBVUSU

КОЛЕБАНИЯ СИЛЫ ВЕТРА ВО ВРЕМЕННОЙ ОБЛАСТИ: ПРИМЕНЕНИЕ ВЕРОЯТНОСТНОГО РАСПРЕДЕЛЕНИЯ ВРЕМЕНИ ОЖИДАНИЯ

Виталь де Жезус Шименес, Абелито Филипе Бело, Коити Симакава

Аннотация. Временная зависимость скорости ветра (СВ), наблюдаемая в областях Восточного Тимора и Японии, анализируется на основе статистического приближения. Гистограмма СВ аппроксимируется распределением Вейбулла в двух различных областях. Причина, по которой гистограмма соответствует распределению Вейбулла, обсуждается с точки зрения обобщения распределения Рэля, которое изначально применялось в отношении рассеивания электромагнитной волны. Также установлено, что плотность вероятности времени ожидания для скорости

ветра, определяемого как время, в течение которого скорость ветра была ниже или выше указанного порогового значения, описывается степенным законом зависимости от времени — $t^{-\alpha}$ ($\alpha < 2.5$), что связано с долгосрочными корреляциями, а не распределением Пуассона. Предложена новая концепция дробной динамики в рамках стохастического анализа СВ.

Ключевые слова: сила ветра, стохастический подход, распределение времени ожидания, распределение Вейбулла, дробная динамика.

Для цитирования: Ximenes, V., Belo, A. F., Shimakawa, K. (2026) Wind power variations in time domain: Introducing a waiting time probabilistic distribution. *Physics of Complex Systems*, 7 (3), 144–151. <https://www.doi.org/10.33910/2687-153X-2026-7-3-144-151> EDN KCMRYU