R E V I E W

Dissertation
„Classical and Quantum Brownian Motion“
submitted for the degree of Doctor of Science
4.2. Chemistry (Physical Chemistry)
by Prof. Roumen Tsekov, M.Sc., Ph.D.

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Biographical notes

Roumen Tsekov obtained master degree "Chemical physics and theoretical chemistry" at 1988 year in the Faculty of Chemistry, Sofia University "St. Kl. Ohridski". In the period 1988-2002, he was assistant and senior assistant, elected at 2009 year for an assistant professor and at 2011 year for a full professor in the Department of Physical Chemistry, Faculty of Chemistry, Sofia University "St. Kl. Ohridski", where he works at the moment. Roumen Tsekov obtained his Ph.D. at 1993 in the field of 4.2. Chemistry (Physical Chemistry) with doctoral thesis "Fluctuation processes at fluid interfaces". Prof. Tsekov published 150 papers and took a part in a number of international scientific conferences and symposiums. He was for long term specializations in University at Buffalo (USA), Technical University Freiberg (Germany), Brisbane University (Australia), invited-professor in University in Cincinnati (USA), University of Tsukuba (Japan), etc.

Overview of the dissertation

The presented Dissertation by Prof. Roumen Tsekov is written in English and summarizes the results from 35 scientific publications of the author in scientific journals with high impact factors. These publications are cited more than 180 times (SCOPUS). Dissertation contains 247 pages – the first 38 pages are summary of the attached full text of all 35 publications. In the proposed publications, Prof. Tsekov is an individual author for 19 publications; he is a coauthor of 16 publications and the first author of 31 publications. These data show the main contribution of Prof. Tsekov in the proposed papers. The number of cited literature is 365 (data from the author), but it is difficult the check this number because the references are given after each attached publication and there is no an updated list of all used references. The Summary of Dissertation is presented in English and Bulgarian and describes the main claims of the author. In fact, the Summary is a copy of the first 38 pages of Dissertation.

Motivation of the study

Quantum mechanics describes the behavior of elementary particles and their physicochemical properties in the micro space. To obtain macroscopic pictures of the studied processes, one uses average global characteristics, which are obtained with the use of statistical mechanics based on the mathematical apparatuses of the theory of probability and stochastic methods. The complexity and generality of these approaches acquire additional assumptions to simplify the problems, solve them and to derive transparent rules. In many cases (even classical), these assumptions are not self-consistent. The aim of the present Dissertation is to describe the relationships between quantum mechanics and Brownian motion – one unsolved general problem in physics and chemistry. To ensure the correctness of introduced therein assumptions, the author reported good quantitative explanation of several experimental data.

Main review of Dissertation and reported results

Prof. Tsekov used a nonstandard way for our country to present his theoretical results in the proposed Dissertation. The literature review is included in the introduction of each attached publication and describes the moment status of the art. The papers are in good journals published after strict review processes and that is why I accept the actuality and the respective new physical insights at the moment of publication. In the introduction of Dissertation, Prof. Tsekov summarizes the well accepted approaches for modeling the Brownian motion from the viewpoint of classical, stochastic and quantum mechanics. From my viewpoint, this part looks like a historical overview – it is not clear what are the contributions of the respective scientists and what is the recent status of the studied problem? The partial answers of these questions the readers can find in the respective separate chapters of Dissertation.

The main part of Dissertation contains three chapters and general conclusions:

Brownian motion of classical particles (the Langevin, Klein-Kramers, and Smoluchowski equations). This chapter summarizes the obtained results in 14 attached publications of Prof. Tsekov [2,3,4,5,6,8,9,11,12,21,22,23,24,30]. One considers the Brownian motion when the subsystem atoms are heavy enough to ignore their quantum nature (called classical particles). It is well known that the detailed description of a system with large number of particles is governed by the Hamilton function. The respective mathematical problem is so complex that it is not possible to solve it in this general formulation. For that reason, one introduces several realistic assumptions to simplify and solve the concrete problems. Prof. Tsekov considers a solid body as the thermal bath, where the bath particles can only vibrate near their equilibrium positions. This assumption leads to one nontrivial generalization of the Langevin equation. In addition, the acoustic phonons in solids are modeled well by the Debye spectrum, which helps one to model the problem with the Markov processes. One important obtained result is that the friction tensor, which is not a constant, depends on the particle positions. In order to clarify the physical nature of the friction tensor, the author discussed a number of particular cases. The developed theoretical approach is applied also for amorphous solids. In the case of Markov processes the evolution of the probability density function is described by the Klein-Kramers equation, which predicts at equilibrium the canonical Gibbs distribution. Prof. Tsekov proves that the evolution of the probability density in configurational space is finally described by the hydrodynamic type of laws: conservation of mass and momentum of the system, in which the configurational entropy is included. The correctness of the developed theoretical approach is confirmed experimentally and leads to quantitative explanation of the resonant diffusion experiments. The generalized Langevin equation is applied also in the case of quantum space, when the force has a nature of a quantum noise. As a result the classical definition of the temperature is generalized to the original temperature operator introduced by Prof. Tsekov. The quantum force is Gaussian and the quantum Klein-Kramers and Smoluhowski equations are direct results from the application of the Furutsu-Novikov- Donsker theorem. If one replaces the termal fluctuations with other natural types of fluctuations (e.g. the locomotion of cells associated with their vitality and active swimming, etc.), then the obtained results can be applied to the Brownian motion of cells, financial markets, etc. after and adequate definition of respective quantities.

Brownian motion and quantum mechanics (Madelung, Wigner-Liouville and Lorentz equations). This chapter of Dissertation summarizes the obtained results in 11 attached publications of Prof. Tsekov [1,19,25,26,27,28,29,30,32,33,34]. The author demonstrates a deep understanding behind the unsuccessful treatment of the quantum mechanics approach to explain the basis of the Brownian motion – the ability of quantum photons to travel freely in vacuum makes the latter a strong dissipative environment. As a result, prof. Tsekov arrives again to Langevin type of equation with a friction force, which does not follow the Markov processes. Because of the stochastic behavior of the quantum mechanics the author found a right way to reformulate the laws for the probability density function in terms of hydrodynamic type of equation analogous to the Madelung approach. This model allows one to describe some peculiarities of the quantum vacuum, for example the thermal free energy should be replaced by the quantum (information) potential. At fast and irregular relativistic trembling of the quantum particles the system jumps to turbulent type regime, which leads to decomposition of the stress tensor to isotropic pressure part and dyadic tensor of local mean turbulent velocity. The last one is simply related to the Fick type of law, therefore the quantum turbulence has Brownian nature. Subsequently, prof. Tsekov extended this idea in the more general case for stochastic dynamics behinds the Wigner-Liouville approach. To give a transparent physical picture, the author starts with the simplest case (the hydrogen atom) and shows the generality of the physical picture for a large number of quantum particles, of course with the more complex mathematical description. Moreover, in the case of point particles Prof. Tsekov introduces a vector multidimensional potential, which is consistent with the quantum theory of filed. The original application of the Euler-Lagrange conditions to the considered system of point particles gives possibility to reduce the problem to one analog of the Lorentz-Langevin equation. The Brownian nature here arises because of the stochastic behavior of the vector potential, where the mean value of the stochastic force is equal to zero. The application of the gauge transformation by the author explains the transport of the interaction potentials by the vector potential. This approach can be considered as a variant of the stochastic electrodynamics. The advantage/disadvantage of this theory should be demonstrated in future theoretical analyses.

Brownian motion and quantum particles (Bohm, Caldeira-Leggett and Master equations). This chapter summarizes the obtained results in 16 attached publications of Prof. Tsekov [1,7,10,13,14,15,16,17,18,19,20,21,25,31,33,35]. Based on the Bohm ideas and the assumption that the quantum particles obey the Newton law for motion under the action of the quantum potential, Prof. Tsekov derives an original functional stochastic equation. This result is from the Bohm-Langevin type and it is represented also in the terms of quantum-hydrodynamic analog for the mean values of the respective quantities. The main advantage is that the hydrodynamic analog is self-consistent and the probability distribution function and mean velocity become a solution of these equations. If one can neglect the nonlinear inertia terms, then one obtains the relationship between the velocity and the probability density function. The subsequent substitution in the continuity equation leads to the “diffusion” equation which includes the Hamilton operator. The author noted that the thermal fluctuations are accounted twice and replaces the quantum potential by the corresponding free energy. As a result Prof. Tsekov arrives to a final result, in which the thermo-quantum equilibrium distribution is a solution. The main question here: is it possible to reformulate initially the general problem in such a way to obtain the correct form of this equation, not to make this not clear replacement at the end of derivation? Prof. Tsekov correctly mentioned that the obtained result is valid in the configurational space and one needs to construct the respective master equation in the subsystem phase space. The solution of this general problem is not known in the literature. For that reason the author obtains original results for structureless environments via spatially averaged friction tensor, in which the friction coefficient is independent on the particle positions. The widely used in the literature Caldeira-Leggett approach has a well-known disadvantage – the predicted equilibrium distribution is not correct. Starting from the Onsager principles, Prof. Tsekov derives a generalization of this equation, in which the matrix of equilibrium Gibbs distribution is a solution (as should be). Because of the nonlinearity of the obtained result the superposition principles are not valid. The author deeply analyzes this result based on partially and full lineal approximations, which prove new or known literature results. Especially, the obtained new theoretical trends need to be confirmed experimentally. From my viewpoint, it is good to see some ideas for these kinds of experiments, which can be used to validate the theoretical predictions.

Review of the author claims in Dissertation

The author claims in Dissertation are formulated in 10 points at pp. 35 and 35 in Dissertation and pp. 39, 40 and 41 in Summary. I accept all of them – they are correct and explain in condensed form the main contribution of Prof. Tsekov in the field. I classify the contributions as follows:

In the field of classical mechanics. The general Langevin equation is derived for an arbitrary mechanical subsystem coupled to harmonic environment of a solid. The obtained original relationship between the friction tensor and interaction potential explains the nonhomogeneity of the friction coefficient in structured environments. The results are applied for adequate quantitative explanation of experimental data of normal alkanes in zeolites. The generality of the developed approaches is demonstrated in the case of Brownian motion of cells, financial markets, etc.

In the field of quantum mechanics. The effect of quantum thermal oscillators on the Brownian motion is accounted for by introduction of the time-acting temperature operator. It allows self-consistent derivations of the Klein-Kramers and Smoluhowski type quantum equations. The theoretical investigation of the Brownian emitter model and the derived evolution equations for the probability density function resolve one of the hypotheses of stochastic electrodynamics that the motion of an electron, swimming in the zero-point vacuum energy fluctuations, leads to the Schrödinger equation. It is proven that the collisions of the target point particles with the quantum force carriers, transmitting the fundamental interactions between the point particles, are the nature behind the Schrödinger equation.

In the field of stochastics applied to quantum mechanics. The obtained Lorentz-Langevin type stochastic equation after original transformation is reduced to the Schrödinger equation. The Brownian motion is described in the frame of Bohmian mechanics. The obtained general nonlinear master equation leads to some important generalizations: new law for the spreading of the wave packet; quantum generalization of the classical Einstein law of Brownian motion; new dissipative models from the Schrödinger and Liouville types.

Comments and suggestions

The proposed Dissertation explains relationships between the Brownian motion and the quantum mechanics. These interrelations are principal for deeper understanding of many processes and theoretical interpretations in physical chemistry, hydrodynamics of complex fluids and many other science areas. The use of the names of famous scientists without citations and analyses of their publications in the first 38 pages of Dissertation does not give information on the assumptions and range of validity of the cited classical results. From my viewpoint, it is important Prof. Tsekov to prepare the monographic book on the considered problems, in which step by step to describe the classical and recent developments in this area so important in theoretical physics and chemistry.

Conclusion

The proposed Dissertation characterizes Prof. Roumen Tsekov as an excellent scientist with own style of work, formulation and solution of complex theoretical problems in physics and chemistry. Dissertation is written by the author, summarizes his contribution in this scientific area and does not contain information and result already published in his Ph. D. Thesis. The present Dissertation and Summary fulfill all regulations of the Law for Academic Staff Development in the Republic of Bulgaria, the Regulations for its implementation and the Internal Rules for the development of the academic staff at Sofia University "St. Kl. Ohridski". Based on my review I give my positive assessment on Dissertation and suggest to Scientific Jury to award the degree of Doctor of Science 4.2. Chemistry (Physical Chemistry) to Prof. Roumen Tsekov, M.Sc., Ph.D.

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27.08.2021

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