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Relaxation and Diffusion in Complex Systems

 Springer

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Preface

Glass transition occurs on cooling or compressing a liquid when the characteristic time of molecular motions responsible for structural rearrangements becomes longer than the timescale of the experiment. As a result, structural relaxation toward equilibrium is arrested below some temperature, T_g , and the material is in the glassy state. This general phenomenon is found in condensed matters of diverse chemical composition and physical structure, and is of interest in research and applications in many disciplines. Considered as one of the many branches of study in physical sciences, glass transition is exceptional in the sense that the problem it presents has a very long history but still not solved till the present time. If one counts from the period of 1854 to 1866 when R. Kohlrausch and F. Kohlrausch in Göttingen, Germany published their scientific studies of relaxation in glassy materials, then the research field of relaxation and diffusion in glasses and liquids is by now about 160 years old. One may even argue that the field is more than two millennia old if starts counting from the days of the Babylonians recording their recipe of making glasses and studies of glasses on stone tablets. It is highly unusual that a problem in physics with such a long history dating back to the dawn of civilization has remained unsolved. Since the last century, many experimental techniques have been invented to macroscopically as well as microscopically examine the properties of glass-forming substances. The database has become so rich that the general and critical facts on glass transition have emerged and are ready for anyone to take into consideration in attempting to solve the problem. There have been many serious attempts to solve the problem throughout the past several decades. The activity is accelerated in recent years by the recognition of the challenge and the fundamental importance of the glass transition problem by many more scientists, Nobel laureates, and even *The New York Times*. Despite the current intensified efforts, it is a general consensus that solution of the problem is still at large, as reported in a 2008 editorial of *The New York Times*.

A modest decrease of temperature can change the viscosity or the structural relaxation time by many orders of magnitude to cause glass transition. The spectacular property germane to glass transition had lured many researchers to focus attention mainly on this experimental fact and to explain the phenomenon expediently by solely focusing on the change in thermodynamic quantities such as

specific volume and configurational entropy. There is a general lack of recognition of the fact that at constant temperature, the intermolecular, interatomic, or interparticle interactions in the glassformer necessarily engender many-body effect in the dynamics of the basic relaxing or diffusing units. The interaction between basic units in glassformers is usually non-trivial and anharmonic, resulting in complex (chaotic) dynamics in the phase space spanned by the coordinates and momenta of the interacting units themselves. One of the major endeavors of this book is to collect multiple facts from experiments as convincing evidences for the presence of the many-body effects in the dynamics that cannot be ignored. To do this, a surrogate for many-body effects has to be used to bring out the evidences from experiments. Perhaps the simplest and the most direct choice of the surrogate is the degree of stretching of the structural relaxation time correlation function $\phi(t)$ beyond the exponential function for non-interacting systems. If the Kohlrausch's stretched exponential function $\phi(t) = \exp[-(t/\tau)^{1-n}]$ is used, then the fractional quantity n appearing in the stretch exponent is a natural choice for the surrogate. An equivalent one is the measured width \mathcal{W} of the frequency dispersion of the susceptibility. Both n and \mathcal{W} are easily accessible from experimental measurements, and they either govern or correlate with the relaxation time τ in its magnitude and its dependences on various parameters at a fixed temperature or on changing temperature. I submit these findings are indisputable evidences for the presence of many-body effects in relaxation and diffusion, which must be incorporated in conjunction with thermodynamic factors into any theory of glass transition. Otherwise, the theory is a failure because it certainly cannot explain the multiple experimental facts indicating that n or \mathcal{W} governs or correlates with the relaxation time τ . Remarkably and surprisingly, in most if not all conventional or popular glass transition theories or models, n or \mathcal{W} does not play any important role and is in some cases not considered at all. This state of affair is one of several reasons why the glass transition problem has not yet been solved.

Unfortunately, relaxation and diffusion in interacting systems, the origin of the many-body effects observed in the glass transition problem, is itself an unsolved problem in statistical mechanics. My encounter with this problem is an example of serendipity in scientific research. By accident, in 1978, I was obliged to attend a seminar on dielectric relaxation of liquids and glass. Prior to 1978, my research was limited to electronic properties using quantum mechanical methods, and I had absolutely no knowledge or appreciation of research in relaxation in classical systems, let alone the glass transition problem. The seminar got me exposed to the research field and stimulated my realization that these interacting systems and many-body effects must be important and necessarily be accounted for in the relaxation and diffusion processes. Since I had no previous knowledge, I was free to think about the problem without any preconceived notion or the influence by established schools of thought. My modest contribution to the problem published in 1979 (known nowadays as the coupling model) yielded predictions of the many-body effects in relaxation and diffusion of interacting systems. The central prediction from the coupling model (CM) equation is general and it spawns many different subsidiary or specific predictions when applied to various processes in different kinds of interacting systems. Despite

the weak theoretical foundation and framework of the original CM, the many predictions it readily offers suggested to me that the best strategy for proceeding was to test these predictions with available experimental data at the outset. If the predictions fail, it would be timely for me to abandon the model and the sojourn in this new area, and return to my previous occupation. To my surprise, the initial tests of the predictions against experiments were successful. After that, I realized that the only way to really test the predictions was to get deeper into the various research fields. This decision forced me to change the course of my scientific career. The continued success of the applications of the CM predictions to increasing areas of research enticed me to explore more areas of application. This had the adverse effect of preventing me from bettering the theoretical foundation of the CM for many years, until more than 15 years later by improvements based on classical chaos, which connects back to the original model based on Gaussian orthogonal ensemble of random matrices, which is related to classical chaos via semiclassical quantization. The central prediction of the CM remains the same for more than 31 years. By no means can the CM be considered as a full solution of the problem of relaxation and diffusion in interacting systems. Notwithstanding, its constructs and predictions are in accord with numerous experiments. Until someone has a better model or theory that can do as much or more than the CM in relation with experiments, I hope I need not to apologize for its shortcomings

The application of the CM to the glass transition problem is natural because glass-forming liquids are just interacting systems belonging to a special class. The voluminous amount of experimental data accumulated over the years on glass-forming substances and systems presents great opportunity of testing the CM predictions. Also there are some occasions where predictions from the CM were made before experiments were carried out, and the results of the experiments were in accord with the forecast. Again the disclaimer must be made that the CM is not a full solution of the glass transition problem, although it accounts well for the many-body effects of the relaxation and diffusion processes, unrivaled by any extant theory of glass transition. One of the constructs in the CM is the primitive relaxation which initiates the evolution of many-body relaxation to reach the terminal steady state of structural relaxation responsible for glass transition. A remarkable achievement of the CM is the realization of the primitive relaxation in experiments by the secondary relaxation of a special kind involving the motion of the entire basic unit of the glass-former. There is a need to distinguish this class of secondary relaxation from the trivial ones. For this purpose, I have called it the Johari–Goldstein (JG) β -relaxation. Not only does this term distinguish the secondary relaxation of the special kind but it also serves to honor these two colleagues for their discovery of secondary relaxation in totally rigid small molecular glassformers, which necessarily involve the motion of the entire molecule. The relaxation time and the properties of the JG β -relaxation are analogous to that of the primitive relaxation of the CM. Like the primitive relaxation, the JG β -relaxation and the structural relaxation are inseparable as evidenced by many relations or connections between the two relaxations found by experiments in glassformers of many different kinds. Hence, the primitive relaxation or the JG β -relaxation plays a fundamental role in the dynamics of glassformers, and no glass

transition theory is complete without considering it and explaining its connection with the structural relaxation. Moreover, there is abundant experimental evidence to show that the primitive relaxation or the JG β -relaxation time is not only sensitive to thermodynamic variables but also a function of exactly the same combination of thermodynamics variables as the primary (structural) relaxation time. From causality, these experimental facts indicate that the dependence of the structural relaxation on thermodynamic variables actually originates from that of the primitive relaxation or the JG β -relaxation, and is magnified in the former by the participation of many units than in the latter. This finding may revolutionize theoretical approaches solving the glass transition problem in the future. There are considerable interests in the early time dynamics manifested by molecules when they are mutually caged by the intermolecular potential. Experimental data also show that this caged dynamics regime is terminated when time becomes comparable to the primitive relaxation or the JG β -relaxation time. This is yet another important role played by the primitive relaxation or the JG β -relaxation time.

If the physics of relaxation and diffusion in interacting systems is general as anticipated by the CM, properties found in the glassformers should show up as analogues in other interacting systems that have nothing to do with glass transition. The final part of the book is devoted to the collection of the experimental measurements and computer simulations to show plenty of analogues of general properties of glassformers in diverse non-glass-forming interacting systems. By the way, this is the reason why in the title of the book I use the term complex systems to include other non-glass-forming interacting systems. The results combined support the existence of universal properties of relaxation and diffusion in interacting systems. It is a very important conclusion because of the following reasons. (1) It identifies a very fundamental problem in physics not pointed out by anyone before that is certainly worthwhile for the theoretical physics community to pursue and provide a solution. (2) The universal phenomena associated with this problem help experimentalists in many different areas of research in relaxation and diffusion in interacting systems (including the glass transition community) to understand their data, especially the anomalies, in the framework of many-body effects caused by interactions and plan more critical experiments. (3) It provides guidance for direction or strategy in application of the systems in technology and industry. (4) The general phenomenology found across different systems in various disciplines and described in the book should provide inspiration for all readers to explore further on their own in this new domain. Throughout the book, the CM is used successfully to rationalize or even quantitatively explain the universal features in the experimental data and to resolve the analogous anomalies found in different interacting systems. The success of the CM suggests it can be used as a basis for others to construct a more rigorous model or theory that is equally or even more successful in explaining experimental findings. Until the time when this more rigorous theory appears in the future, the CM is a useful tool to solve problems of relaxation and diffusion in interacting complex systems encountered in the future. The reader may be as surprised as I am that such a simple CM equation is applicable to so many different systems and problems. If this CM equation withstands the test of time and can be considered as truth at least to

some degree, then the quote from Lord Byron, “For truth is always strange; stranger than fiction,” seems fitting to describe the situation.

A major part of this book has been to collect the results of many experimental investigations cited in more than 1800 references. Only part of these is reflected in the few hundred figures selected. Without this large collection of experimental data, there would have been no way for me to bring out the universal behavior of relaxation and diffusion in interacting systems, and test the CM predictions. Therefore I salute all the experimentalists who have contributed to the advancement of our knowledge in this new exciting area.

In some sections of the book, connections of the basic physics are made to practical problems encountered in various technological areas and industries. Examples include the problem of improved solubility and bioavailability of pharmaceuticals, the stabilization of lyophilized biopharmaceuticals used in medical treatments, hydration of biomolecules for functioning in life science, fuel cell materials for the energy industry, and novel materials for improved performance in applications. I show that the basic features of dynamics of the systems in these other fields are isomorphic to glassformers, which is perhaps unsurprising because they are all interacting systems and the same physics of many-body relaxation and diffusion basically governs their behavior. I have demonstrated that the understanding of the relaxation and diffusion properties of prototypical glass-forming systems and substances gained has benefited some progress in these applied research fields important for the populace and the economy worldwide, and I expect it will bring more benefits in the future by more cross-field fertilization.

Considering many of the substances and systems discussed in this volume are so complex and widely different in chemical composition and physical structure, it is remarkable that universal properties of relaxation and diffusion exist and are shared by all of them. It seems to be the consequence of another unexplored fundamental physical law of Nature for irreversible processes in interacting systems. Only in the presence of a physical law can universal behavior be coming out from diverse condensed matter and systems. Capturing this physical law is a worthwhile scientific endeavor of the new century.

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Washington, District of Columbia

K.L. Ngai

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