



Perspectives on the scientific career and impact of Prabhat K. Gupta

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ABSTRACT

This special issue is devoted to celebrating the scientific career and impact of Prof. Prabhat K. Gupta, the 2018 winner of the Sir Nevill F. Mott Award from the *Journal of Non-Crystalline Solids*. While the rest of this issue focuses on the latest groundbreaking research in topics related to Prabhat's research interests, in the current article we look back and review some of the remarkable research achievements and impact that Prabhat has had over his career. Prabhat is known for his deep and thoughtful approach to a wide range of topics in both experimental and theoretical glass science, with particular emphasis on glass structure and topology, thermodynamics, and kinetic processes including diffusion, relaxation, and crystallization. In this article, the three authors each offer their own perspectives on the impact and legacy of Prabhat's research.

1. Act I: Early years (by A. K. Varshneya)

Prabhat's career in glass science started in 1966 (a year after my arrival) as a graduate student at Case Western Reserve University, Cleveland OH, under the advisorship of the late Professor Alfred R. Cooper. Right from the start it became clear that the two were seriously inclined towards adding scientific rigor to analyzing problems in glass. His earliest publication [1] was based on simulation of spinodal decomposition in a binary system (Al-Zn taken as an example). This was research conducted by a bright, computer-savvy, undergraduate student, Lee Swanger, and was essentially guided by Prabhat. In a well-disciplined approach following Al Cooper, Prabhat converted the one-dimensional nonlinear differential equation of interdiffusion to an equation with dimensionless variables and a time constant. One parameter used chemical and mechanical interaction energy relative to the thermal energy, and the second compared a gradient energy relative to thermal energy. The time constant was then written in terms of the two parameters and the particle mobility. It was possible to show that, although a linearized approximation of the differential equation was sufficient to give a good representation of the results, the nonlinear terms were necessary to demonstrate the composition fluctuations to go across the spinodal boundary. It was also possible to show how fluctuations can divide into smaller wavelengths or can grow into larger wavelengths. This simulation was essentially a step forward beyond the work by Hillert [2], Cahn and Charles [3], and DeFontaine [4]. The thermodynamics of spinodal separation was clear once the math was

sorted out.

This paper was soon followed by a publication [5] on the handling of finite electron beam diameter in an electron microprobe analyzer where rapidly changing concentration in a specimen (e.g., across a sharp boundary) would get convoluted with the size of the sample probing beam. The deconvolution procedure of a measured concentration function to its true variation was straightforward using Fourier analysis if one obtained the beam intensity function (instrument function) separately. Up to that point, most people simply engineered their data (manually sharpened the distribution of x-ray counts versus distance curve) by guessing.

The [D]-matrix paper [6] could perhaps be considered a truly remarkable contribution towards the understanding of multicomponent diffusion in materials using linear algebra. It was inspired by my earlier publication on diffusion in a ternary silicate glass [7]. The three of us (Al Cooper, Prabhat and I) had attended a linear algebra course in the mathematics department and armed ourselves with newer confidence. Whereas I developed the linear algebra approach to describe uphill diffusion along the diffusion paths in a K_2O - SrO - SiO_2 ternary composition diagram type figure, Prabhat correctly argued that, for an n -component system, one only needed $n-1$ independent equations relating the flux to the concentration gradients through a symmetric interdiffusion coefficients matrix [D]. Thus, for a 3-component system, the presentation, being a 2×2 matrix, required only three independent interdiffusion coefficients (the two conjugate terms along the diagonal of the matrix, and the one coupling term). Since Onsager's reciprocal

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relations are obeyed, and the entropy production must be positive in the transport process, the $[D]$ matrix must have positive eigenvalues and be diagonalizable. This results in a unique description where rules of interdiffusion could be described using linear algebra. Conditions for straight-line diffusion or uphill diffusion could be readily worked out.

2. Act II: The glassy state, relaxation, and crystallization (by E.D. Zanotto)

After completing his Ph.D. with Al Cooper at Case Western Reserve University in 1972, Prabhat spent a year as a post-doc with famed statistical mechanics expert Joel Lebowitz at Yeshiva University. Prabhat then joined Catholic University as an adjunct faculty member. He was later hired by Owens Corning as a Senior Scientist from 1977 to 1986. Following this stint in the fiberglass industry, Prabhat became an Associate Professor at The Ohio State University in 1986, where he spent the rest of his career. Prabhat was promoted to full Professor in 1990, retiring as an Emeritus Professor in 2012.

Prabhat is the winner of numerous awards and honors from the glass community. He is a Fellow of both the American Ceramic Society (1986) and the Society of Glass Technology (2009). In 1993, Prabhat was awarded the prestigious Otto Schott Research Award for “outstanding work in the field of basic research and application for glasses and glass-ceramics.” His most recent awards include the George W. Morey Award from the American Ceramic Society (2009, see photo in Fig. 1), the Toledo Glass and Ceramics Award (2011), and the Sir Nevill F. Mott Award from the *Journal of Non-Crystalline Solids* (2018), which “recognizes a distinguished senior scientist with a history of outstanding contribution to the science of non-crystalline solids over many years.” A photo from the Mott Award ceremony in San Antonio, Texas, is provided in Fig. 2. In the remainder of this article, we focus on reviewing several of Prabhat's most significant and impactful contributions to glass science.



Fig. 1. Prabhat K. Gupta and wife, Jyoti Kamal, after Prabhat received the George W. Morey Award during the 8th Pacific Rim Conference on Ceramic and Glass Technology in Vancouver, Canada (2009).



Fig. 2. Photograph from the 2018 Sir Nevill F. Mott Award ceremony at the Glass and Optical Materials Division meeting of the American Ceramic Society in San Antonio, Texas. From left to right: Karine van Wetering (publisher, *Journal of Non-Crystalline Solids*), B. G. Potter, Jr., Josef Zwanziger, Edgar D. Zanotto (editors, *Journal of Non-Crystalline Solids*), and Prabhat K. Gupta (winner of the Mott Award).

2.1. Glass vs. amorphous solids

In an educational article published in 1996 [8], Prabhat Gupta suggested that non-crystalline solids (NCS) can be divided into two thermodynamically distinct classes: glasses and amorphous solids (α -solids). He argued that these two types of materials show distinct structural correlation with their liquids and behave differently upon heating. Based on Zachariasen's notion of glass as a topologically disordered network, with short-range order (SRO) equivalent to that in the corresponding crystal, he proposed structure-based definitions for glasses and α -solids. Gupta suggested an extension of Zachariasen's ideas for good glass forming ability, i.e., a good non-crystalline former should satisfy two conditions:

1. SRO (NCS) = SRO (crystal); and
2. The NCS should be topologically disordered.

If either one of these conditions is violated, then the system is a poor NCS former. He gave examples, such as KCl (an extremely reluctant glass former) where the coordination number (CN) of Cl around K is approximately 4 in the liquid and is 6 in the crystalline form. According to Gupta, a NCS is a glass if it satisfies a third condition.

3. SRO (glass) = SRO (liquid)

This condition is clearly satisfied for glassy materials formed by melt-quenching because the structure of the melt is (temporarily) frozen-in during the glass transition. However, this condition is independent of the method of formation. Amorphous solids were defined as NCS that violate the third condition above. Well-known examples are α -Si and α -Ge. They are good NCS formers because the coordination numbers in the amorphous and crystalline states are the same (CN = 4). However, they violate condition (3), because in the liquid state CN > 4. Unlike glasses, amorphous solids do not show structural relaxation towards the supercooled liquid (SCL) state; in other words, they do not show a glass transition. This concept implies that

amorphous solids cannot be made by quenching a liquid; they can only be formed by other methods, such as vapor deposition, mechanical alloying or destruction of crystals by high energy. If an α -solid could be made by quenching a liquid, it would have to undergo a glass transition, and would then become glass. Besides, when they are adequately heated, glasses usually relax to the SCL state before crystallizing, whereas α -solids crystallize without relaxing.

2.2. Structural basis of glass relaxation

In 1985, while working at Owens Corning, Gupta and coworkers Phil Bray and Ming Lui published a well-designed, definitive study, which was summarized in a single page [9]. In that work, they measured the refractive index and the fraction of four-coordinated boron by nuclear magnetic resonance (NMR) in rapidly cooled (10 μm fibers) and in their annealed counterparts both made of an aluminum borosilicate glass. Hence, samples of the same glass underwent different thermal histories that lead to widely different fictive temperatures, estimated to be 1200 K (as made fiber) and 950 K (annealed).

The fraction of four-coordinated boron increased from 10% in the rapidly cooled fiber to 16% in the same fiber after annealing, and the refractive index also increased. The index of the original fiber was 1.557, whereas that of the annealed fiber agreed with the bulk glass (1.562). Crystallization was not observed in the annealed fiber. The authors concluded that boron coordination is temperature dependent and associated with structural relaxation. Their results provided the first definitive support to a theory proposed by Leko and Mazurin [10] that coordination equilibria can be considered as a basis for interpreting structural relaxation in glasses.

2.3. Enthalpy relaxation of glass

In a subsequent study in 1992 [11], Gupta and his coworker J. Huang designed, conducted, and analyzed a series of revealing experiments about the enthalpy relaxation process in glass. Enthalpy relaxation in rapidly cooled soda lime silicate (NBS 710) glass fibers of 8–12 μm in diameter was compared with relaxation in slowly cooled bulk samples of the same composition. Their main idea was to examine relaxation in systems far from equilibrium (very thin fibers with high fictive temperature) through an investigation in terms of the Tool-Narayanaswamy (TN) model of nonlinear relaxation.

Their analysis clearly showed that, while the TN model describes the results on bulk samples well, it is inadequate for describing relaxation in rapidly cooled fibers. This landmark research pointed out to the insufficiency of the TN model for systems far from equilibrium and paved the way for the development of other relaxation models (to be discussed in Section 3.7).

2.4. Do cathedral glasses flow?

A popular urban legend concerns the apparent flow of stained glass windows in medieval cathedrals, where the glass windows are commonly observed to be thicker at the bottom than they are at the top. Is glass a liquid or is it not? The three authors of the current article have been asked this question throughout the past few decades by students, colleagues, and acquaintances since they have heard at school or read in encyclopedias or science textbooks that medieval cathedral windows are thicker at the bottom, which would suggest a downward flow of glass at room temperature. It appears that this alleged flow of ancient window glasses still merits clarification.

In 1997, I was discussing this issue in a physics meeting, when I was challenged by two theoreticians to prove that old glass windows do not relax and flow within a timespan of a few centuries. I accepted the challenge and started to dig into the literature because I was almost sure to find some publications on the subject; however, to my surprise, none was found. Therefore, I decided to carry out a “back of envelope”

estimate on the glass relaxation time at room temperature. The idea at that time was to find a strong (Arrhenian) liquid with a glass transition temperature (T_g) approximately equal to that of (highly non-Arrhenian) soda lime silicate window glasses, as a proxy. Bingo! I found GeO_2 glass, for which T_g is $\sim 550^\circ\text{C}$. The viscosity of a typical GeO_2 glass is given by $\log \eta = -9.94 + 17,962/T$ (with η in Pa·s and T in K). This Arrhenian viscosity equation allowed extrapolation down to room temperature. In this way, the estimated characteristic relaxation time, $\langle \tau_r \rangle = \eta/G_\infty$, at room temperature was 10^{32} years. The conclusion was that GeO_2 glass (and, inferentially window glass) might relax and flow at room temperature over only incredibly long times [12].

Prabhat was among those who read the article with interest and contacted me proposing that he could try to perform a similar estimate for soda lime silicate glass. He also pointed out that the use of isostructural viscosity, i.e., the viscosity of the glassy state when the structure is temporarily frozen, instead of the equilibrium viscosity, extrapolated to room temperature should give a more realistic estimate of the relaxation time. Using relaxation and isostructural viscosity data from the literature, the resulting calculated relaxation time was 10^{24} years [13]. Even though this revised relaxation time was several orders of magnitude smaller than that for GeO_2 glass, it supported the conclusion that window glass cannot flow at room temperature in a human time scale.

In a recent study, Gulbitten et al. [14] investigated the dynamics of a medieval glass composition used in Westminster Abbey, UK. Depending on the thermal history of the glass, the estimated room temperature viscosity is on the order of 10^{24} to 10^{25} Pa·s, many orders of magnitude lower than found in the previous study of soda lime silicate glass [13]. This measurement was in quantitative agreement with a new model for the (nonequilibrium) viscosity of glass (see Section 3.7). Using analytical expressions to describe the glass flow over a wall, they also calculated a maximum flow of 1 nm over a billion years. Hence, despite this significantly lower value of the room temperature viscosity, the viscosity of the glass is much too high to observe measurable viscous flow on a reasonable timescale. Therefore, glasses with a T_g on the order of ~ 500 – 600°C might flow at room temperature only on geological timescales; on the other hand, glasses having a T_g close to room temperature definitely flow within a few hours or days.

2.5. Crystallization work in Brazil

In 2015, Prabhat spent a sabbatical period of 3 months at the Vitreous Materials Lab (LaMaV - CeRTEV) at the Federal University of São Carlos, Brazil, where he worked intensively with me and my post-doctoral fellow, Daniel R. Cassar. During his stay with us, he delivered a well-attended graduate level course on “Glass transition and relaxation”, available online at <https://youtu.be/CCgsRGO2etg>, and we worked together on some fundamental problems regarding homogeneous crystal nucleation in glasses and supercooled liquids, which resulted in the new research described below.

The collaborative research between Prabhat and my group [15] focused on calculating the location of the temperature of maximum (homogeneous) nucleation rate, T_{max} , as a function of the glass transition temperature. The colossal failure of the classical nucleation theory (CNT) in predicting absolute values of crystal nucleation rates in glass-forming liquids has been well documented [16]. This failure is likely a direct result of the lack of knowledge about two of the most important physical properties involved in the nucleation process: the values of crystal nucleus/liquid interfacial energy, σ , and the diffusion coefficient controlling bond breaking and rearrangement at the nucleus interface, $D^*(T)$. It is challenging to independently measure these two parameters in glass-forming substances. Therefore, several assumptions are usually made in using or testing the CNT. Efforts have been directed towards testing predictions of CNT for nucleation features that do not involve magnitudes of the nucleation rates. The temperature where the reduced nucleation rate is maximum, T_{max}/T_m (where T_m is the melting point),

is one such feature of particular interest because it can be measured experimentally with good precision. An understanding of and ability to predict T_{\max} is also useful for the design of nano-structured glass-ceramics [17]. Questions such as “How does T^* vary with system parameters?” and “How these observations compare with predictions of CNT?” are, therefore, of much interest.

Therefore, in 2016, Gupta et al. [15] derived a rigorous expression for $T^* = T_{\max}/T_m$ (as a function of T_g) based on CNT in combination with the Stokes-Einstein relation and the Vogel-Fulcher-Tammann (VFT) equation for $D^*(T)$ under three conditions: constant activation energy of atomic transport, constant VFT temperature, and constant fragility. The resulting calculations were tested against experimental nucleation data for several stoichiometric oxide glass formers.

The overall conclusion was that, despite its shortcomings in predicting the magnitudes of the steady-state nucleation rates, CNT might be quite useful for the analysis of other features of the nucleation process. For example, the equations derived in [15] and associated calculations show that, when combined with experimental viscosity data and calculated values of the thermodynamic driving force and interfacial energy, CNT predicts that T^* increases (and the magnitudes of nucleation rates decrease) with increasing the reduced glass transition temperature, T_g/T_m . They also indicate that T^* increases with an increase in the liquid fragility (for a given value of the normalized thermodynamic barrier). The results also support the experimental observation that homogeneous nucleation is less likely to be observed in glasses with $T_{\max} < T_g$.

2.6. Relaxation and crystallization

When undercooled below its melting or *liquidus* temperature, T_m , a liquid becomes *metastable* with respect to the stable crystal and, at the same time, *unstable* with respect to the “structurally relaxed non-crystalline state” called the supercooled liquid (SCL). Thus, two different processes may take place simultaneously in a melt cooled below T_m : structural *relaxation* leading to the SCL, and crystal *nucleation* leading to the stable crystal. The importance of these two processes in glass science and technology cannot be overstated [18]. While avoidance of crystal nucleation is the very essence of glass formation, controlled nucleation is a key step in the production of advanced glass-ceramics [19]. Similarly, the development of structural relaxation underlies the liquid-to-glass transition, where a SCL falls out of (metastable) equilibrium due to a finite observation (experimental) time and temporarily freezes into a non-equilibrium vitreous state called glass [18]. Naturally, much effort has been invested towards understanding both relaxation and crystal nucleation processes, and the progress made thus far has been reviewed in excellent publications that will not be discussed here.

In Ref. [20], Gupta and co-workers took as an example experimental homogeneous nucleation rates in the lithium disilicate ($\text{Li}_2\text{O}\cdot 2\text{SiO}_2$) supercooled melt—a liquid that is moderately strong, stoichiometric, and is known to nucleate homogeneously [21]—to show the failure of CNT at low temperatures. Such failure is indeed seen in a linearized plot in Fig. 3, where after combining with the experimentally measured nucleation time-lag data, τ , nucleation rate data are plotted in terms of the variation of $\ln \left[\frac{I(T)\Delta G_v^*(T)\tau(T)}{\sqrt{T}} \right]$ versus $\frac{1}{T\Delta G_v^*(T)}$, where ΔG_v is the free energy/volume difference between the crystal phase and the SCL. According to the CNT [20–21], such a plot should be linear with a negative slope, which is related to the crystal-liquid interfacial energy. CNT fits the data quite well in the high temperature region, however, in the low temperature region, the measured rates drop off markedly compared to the extrapolation of the high temperature CNT fit.

Other explanations have been proposed for the CNT break at $T_{\max} \sim T_g$ (which is not related to the breakdown of the SE equation), always treating the SCL liquid as being chemically and structurally homogeneous. In a distinct, original perspective, Gupta et al. [20]

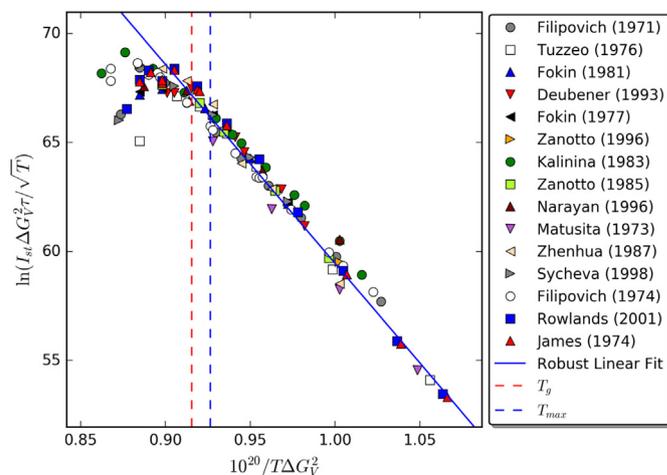


Fig. 3. Linearized plot of $\ln \left[\frac{I(T)\Delta G_v^*(T)\tau(T)}{\sqrt{T}} \right]$ versus $\frac{1}{T\Delta G_v^*(T)}$ for the $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ system using experimentally determined values of $I(T)$, nucleation time-lags, $\tau(T)$, and thermodynamic driving force, $\Delta G_v(T)$ from several authors. The failure below T_g is clearly shown. Reprinted from Ref. [20] with permission.

treated crystal nucleation in a non-uniform medium. For that purpose, they used a novel concept advanced by Stevenson and Wolynes [22]. Based on the dynamically heterogeneous nature of supercooled liquids, these authors proposed the existence of a “cross-over” temperature, T_X , that might control the lower limit for the validity of CNT.

T_X is defined as the temperature where the size scales of the relaxation and nucleation processes become equal, $\xi(T_X) = r_c(T_X)$, where $\xi(T)$ is the average size of the cooperatively rearranging regions (CRR) that characterizes the size scale of relaxation in a dynamically heterogeneous liquid, and $r_c(T)$ is the size of the critical crystal nucleus based on CNT, which defines the nucleation size scale. T_X has a thermodynamic origin, and theoretically, it must exist between the Kauzmann temperature (T_K) where the CRR size is (incorrectly) presumed to diverge, and T_m , where the critical nucleus size diverges. The cross-over of the two characteristic sizes poses an interesting question for the mechanism of crystal nucleation below T_X . Since structural rearrangements on a scale smaller than $\xi(T)$ cannot take place because they are configurationally constrained by the interactions with the surrounding frozen environment, how can such a region undergo structural changes required for a crystal to nucleate?

Stevenson and Wolynes [22] showed that for the molecular glass formers *o*-terphenyl and methanol the calculated values of T_X are close to their glass transition temperatures, T_g . In Ref. [20], Gupta et al. examined the low temperature regime ($\leq T_{\max}$) of nucleation kinetics in lithium disilicate. Using experimental data, they reported the first-ever values of T_X for an inorganic glass-former. The results show that T_X is nearly equal to the temperature where the nucleation rate is maximum, T_{\max} .

Therefore, in Fig. 4 [20], Prabhat and co-workers have shown that the cross-over temperature for supercooled lithium disilicate is close to the temperature of maximum nucleation rates. Based on that finding, they suggested that the abnormal decrease in nucleation rates below the cross-over temperature is most likely because, in this regime, the size of the CRR controls the critical nucleus size and the nucleation rate, hence the nucleation mechanism most likely changes around T_X . To the best of our knowledge, this finding linked, for the first time, measured crystal nucleation kinetics to *dynamic heterogeneities* in a supercooled liquid, offering new opportunities towards the understanding of the nucleation phenomenon. However, the breakdown of CNT at T_g is still an open problem that is currently being pursued by several research groups. It would be relevant to extend this type of test to other glass-forming systems to generalize (or not) the above reported findings.

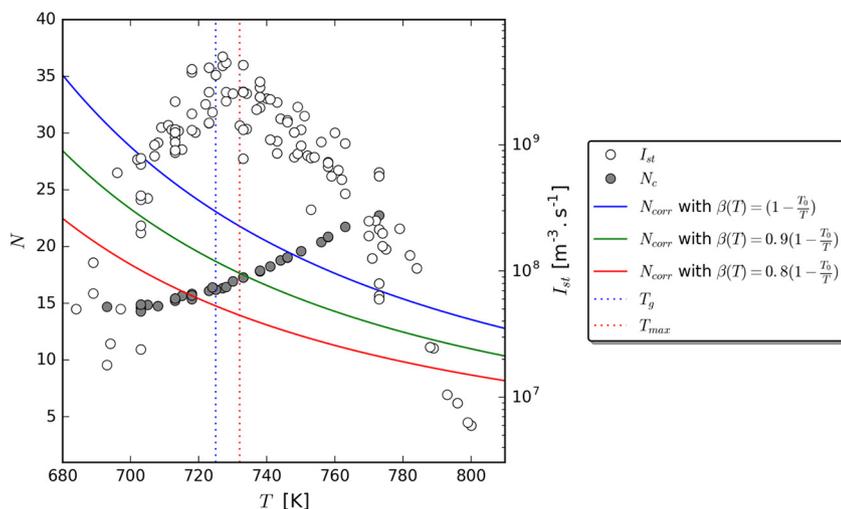


Fig. 4. $N_c(T)$ and $N_{corr}(T)$ versus temperature. N_c = calculated number of atoms in the critical nucleus using experimental nucleation rates and CNT. N_{corr} = estimated number of correlated units in the cooperatively rearranging region. Upper, average, and lower bounds are shown. I_{st} = experimental steady-state nucleation rates reported by several authors for lithium disilicate. The two vertical lines indicate the temperature T_{max} (~732 K) where the nucleation rate is maximum, and the glass transition temperature, T_g (~725 K), as defined by a viscosity of 10^{12} Pas. Reproduced with permission from Ref. [20].

2.7. Kinetic spinodal temperature

That same study by Gupta et al. [20] triggered the idea of experimentally testing the concept of the *kinetic spinodal* temperature, T_{KS} . A key assumption underlying the current macroscopic understanding of relaxation and nucleation is that the time scales associated with these two processes—the relaxation time, $\tau_R(T)$, and the nucleation time, $\tau_N(T)$ —are vastly different so that the two phenomena can be treated independently. This assumption is certainly true at temperatures just below the melting point, where the relaxation time is much less than the nucleation time, allowing the liquid to be treated as a SCL before nucleation begins. However, with decreasing temperatures, approaching T_g , the two different time scales approach each other and the assumption regarding the separation of time scales becomes increasingly more dubious, and the failure of the CNT becomes more pronounced [20].

In his classic paper, Kauzmann [23] hypothesized that the two time scales cross at a temperature known as the *kinetic spinodal* temperature, i.e., $\tau_R(T_{KS}) = \tau_N(T_{KS})$. T_{KS} is considered the “lower metastable limit” or the “homogeneous nucleation limit” of a SCL below which nucleation is inevitable and the supercooled liquid state does not exist. Clearly, if T_{KS} exists, it also marks a lower limit for the validity of the classical nucleation theory. In addition, if $T_{KS} > T_K$ (the Kauzmann temperature) the entropy paradox predicted by Kauzmann cannot take place because any SCL would nucleate (crystallize) at a higher temperature before reaching that state! However, the existence of T_{KS} had only been clearly shown in a MD simulation of a high-pressure form of silica glass [24]. Hence it remained questionable because it had not been demonstrated experimentally. Preliminary estimates made in the Gupta-Cassar-Zanotto paper [20] stimulated a thorough study that was later published by his co-authors, Zanotto and Cassar [25]. They focused their attention on selected compositions of the two most important oxide glass-forming systems, a borate and a silicate, which show measurable homogeneous crystal nucleation in laboratory time scales. For both materials, they found that the T_{KS} are significantly higher than the predicted T_K . Therefore, at ambient pressure, at deep supercooling before approaching T_K , crystallization wins the race over structural relaxation. Hence, at least for these important representative compositions of the silicate and borate glasses, the temperature of entropy catastrophe cannot be reached; it is averted by incipient crystal nucleation at a higher temperature. Moreover, the notion of diverging dynamics at a (hypothetical) Kauzmann temperature cannot be physically realistic, since any liquid at finite temperature must have a finite (not infinite) viscosity: *there is always some nonzero probability that the activation barrier for viscous flow can be overcome at any finite temperature.*

3. Act III: Constraint theory, ergodicity, entropy, viscosity (by J.C. Mauro)

Throughout my career, I have had the distinct pleasure of learning from two of the world's most celebrated glass scientists—who also happen to be first cousins! My academic father, Arun K. Varshneya, taught me through all my student days at Alfred University (B.S. and Ph.D. degrees in glass science), and he remains my “glass guru” all these years later. My interactions with Prabhat Gupta began shortly after the publication of my first article with Arun on modeling of glass transition behavior [26], which captured Prabhat's attention and led to many fruitful discussions and later collaborations. Through many years of mentoring and close collaboration, Prabhat became my “academic uncle” and truly a second advisor to me. In this section, I will review and briefly discuss the impact of several of Prabhat's papers relating to our work together.

3.1. Random pair model of borate glasses

Prabhat's pioneering work in the topological principles of glass formation dates back to the 1980s. At the 14th International Congress on Glass (ICG) in New Delhi, India, Prabhat presented a paper proposing the “random pair” model for the structure and topology of borate glasses. Although never published in a standard journal, this proceeding from the ICG meeting has become a classic in the field of borate glasses [27].

The structure of borate glasses has been an especially interesting topic for glass scientists owing to the so-called “boron anomaly,” where the addition of modifier ions can lead to two distinct and opposing effects: (a) the conversion of boron from trigonal to tetrahedral coordination, increasing the connectivity of the network, or (b) the creation of non-bridging oxygen, which ruptures the linkages between cations and decreases the connectivity of the network. The random pair model successfully quantifies the fraction of tetrahedrally coordinated boron as a function of modifier content. It is based on the following three rules:

1. Tetrahedral BO_4 groups occur in corner-sharing pairs, where the angle between the BO_4 groups is random.
2. Pairs of BO_4 tetrahedra cannot be bound to each other.
3. Non-bridging oxygens occur in trigonal BO_3 groups only, and not in BO_4 groups.

These rules effectively set up the topological conditions for BO_4 formation in borate glasses. Upon initial addition of modifiers to B_2O_3 glass, pairs of BO_4 groups form without the creation of non-bridging

oxygens (NBOs). However, upon reaching 50% of the total boron population, BO_4 cannot continue to form, owing to the second rule above. Consequently, further addition of modifiers requires the formation of NBOs on the BO_3 groups, which also reduces the number of BO_4 groups, since the number of bonds available to BO_3 groups decreases as a result of NBO formation. In addition to offering accurate predictions of boron speciation in borate glasses, the random pair model has been successfully extended to predict boron speciation in borosilicate glasses, where the pairs of BO_4 groups can also bond to SiO_2 tetrahedra [28]. Recently, the presence of a significant fraction of linkages between pairs of BO_4 groups has been experimentally confirmed by Yu et al. using double-quantum ^{11}B NMR spectroscopy [29].

3.2. Fictive temperature and fictive pressure

As a nonequilibrium material, glass requires additional order parameters to describe its thermodynamic state. Historically, this was accomplished using a single fictive temperature, T_f , or (later) a multitude of partial fictive temperatures, accounting for the distribution of relaxation times that occur during the glass relaxation process [30]. In 1988, Prabhat published an article on “Fictive pressure effects in structural relaxation” [31], where he derived a model for the relaxation behavior of glass in terms of both a fictive temperature (T_f) and a fictive pressure (P_f). Based on classic Onsager irreversible thermodynamics, the model showed that coupling between T_f and P_f effects can lead to non-monotonic structural relaxation, even under isobaric conditions.

The coupling of fictive temperature and fictive pressure effects offered important insights into glass relaxation physics. However, a subsequent study together with Roger Loucks and myself [30] showed that it is not generally possible to describe the nonequilibrium state of a glass in terms of any combination of equilibrium states. In other words, the very concepts of fictive temperature and fictive pressure are fundamentally flawed; even a continuum of T_f and P_f values is insufficient for capturing the true thermodynamic state of a glass. The glass science community is still awaiting a solution to this important problem. When this solution comes, it will no doubt be inspired by Prabhat's pioneering work in this area.

3.3. Rigid polytope model of glass topology

Prabhat's advisor at Case Western Reserve University, Al Cooper, was a devoted follower of Zachariasen and his random network theory of glass structure [32]. Zachariasen's random network theory generated significant controversy for decades, most notably from Lebedev's group in the Soviet Union [33]. Al Cooper's admiration for Zachariasen, both as a man and as a scientist, was evident in his beautiful tribute article, “W.H. Zachariasen—The melody lingers on,” published in 1982 [34].

Cooper recognized that Zachariasen's rules are more than just guidelines for the structure of glass: they are actually topological rules governing whether it is possible to make an infinitely large, topologically disordered network in three-dimensional space [34]. Building upon the seminal work of Zachariasen, Gupta and Cooper derived a general mathematical condition for when it is possible to construct such a network [35–36].

The Gupta-Cooper model considered glass as a network of rigid polytopes in a space of arbitrary dimensionality. The rigid polytopes are connected at their vertices to construct the disordered glassy network. The Gupta-Cooper approach thus presents a completely general topological condition for whether a glass network can be constructed—an insightful culmination of the topological view of glass formation originally proposed by Zachariasen more than a half-century earlier (in 1932) [32].

3.4. Temperature-dependent constraint theory

While Gupta and Cooper formulated a topological description of

glass in terms of a network of rigid polytopes [35–36], Phillips and Thorpe adopted an atomic-scale approach for their treatment of glass topology [37–38]. The Gupta-Cooper and Phillips-Thorpe approaches to glass topology are mathematically equivalent, both predicting the same rigidity percolation in threshold for optimized glass formation. While both approaches can account for the composition dependence of glass network rigidity, neither approach had considered the temperature dependence of the bond constraints. In other words, both the Gupta-Cooper and Phillips-Thorpe models implicitly assumed zero temperature conditions.

The notion of temperature-dependent constraints was originally proposed by Prabhat in a 2007 paper with Dan Miracle concerning glass-forming ability in metallic glass-forming systems [39]. The following year, temperature-dependent constraint theory was fully developed and formalized during a highly productive summer “sabbatical” in my group at Corning Incorporated. The Gupta-Mauro temperature-dependent constraint theory [40–41] opened a completely new field of study within the glass modeling community. Together, we showed that temperature-dependent constraint theory can provide quantitatively accurate predictions of glass transition temperature and fragility, two of the most important properties governing glass formation. A wide range of researchers quickly followed suit, applying temperature-dependent constraint theory to a variety of glass chemistries [42–48], extending the theory to predict new properties [28,49–52], and connecting temperature-dependent constraint theory to other modeling approaches such as molecular dynamics [53]. Temperature-dependent constraint theory has also been successfully applied towards the development of new industrial glasses, including Corning Gorilla® Glass [54–55]. Comprehensive reviews of recent advances in the field are available by Mauro [56], Micoulaut [57], and Smedskjaer et al. [58]

3.5. Broken ergodicity and the glass transition

One of the defining features of the glass transition is the breakdown of ergodicity that occurs as the equilibrium (ergodic) liquid is frozen into the nonequilibrium (non-ergodic) glassy state. The statistical mechanics (and thermodynamic implications) of broken ergodicity were first developed by Palmer in 1982 [59]. Palmer considered the breakdown of ergodicity as a discontinuous process, i.e., a sudden transition from an ergodic to a non-ergodic state.

Of course, in real systems (such as during laboratory glass formation), the breakdown of ergodicity does not occur suddenly at a single point in time. Rather, there is a *continuous* breakdown of ergodicity as the internal relaxation time scales in a system gradually become longer than the experimental (observation) time scale. The concept of *continuously broken ergodicity* was first developed by Mauro, Gupta, and Loucks [60] based on conditional probabilities in an arbitrary energy (or enthalpy) landscape. With continuously broken ergodicity, the statistical mechanics of glass-forming systems can be described in both the fully ergodic (liquid) and fully non-ergodic (glassy) states, and throughout the entire glass transition regime. As such, continuously broken ergodicity serves as the foundation for a complete statistical mechanical and thermodynamic treatment of glass-forming systems [61].

In addition to its scientific importance for describing the fundamental physics of the glass transition, continuously broken ergodicity enabled the derivation of a master equation approach for accessing long time scales for the calculation of glass relaxation [62]. The methodology involves dynamically grouping the basins of an energy landscape into *metabasins* satisfying the condition of internal ergodicity, i.e., within a metabasin the dynamics are fast enough to achieve local equilibration on the experimental time scale. Consequently, the full set of master equations describing the inter-basin dynamics can be reduced to a reduced set of master equations describing the slower inter-metabasin dynamics. After the probability of each metabasin is determined from the master equations, the probability of occupying each individual

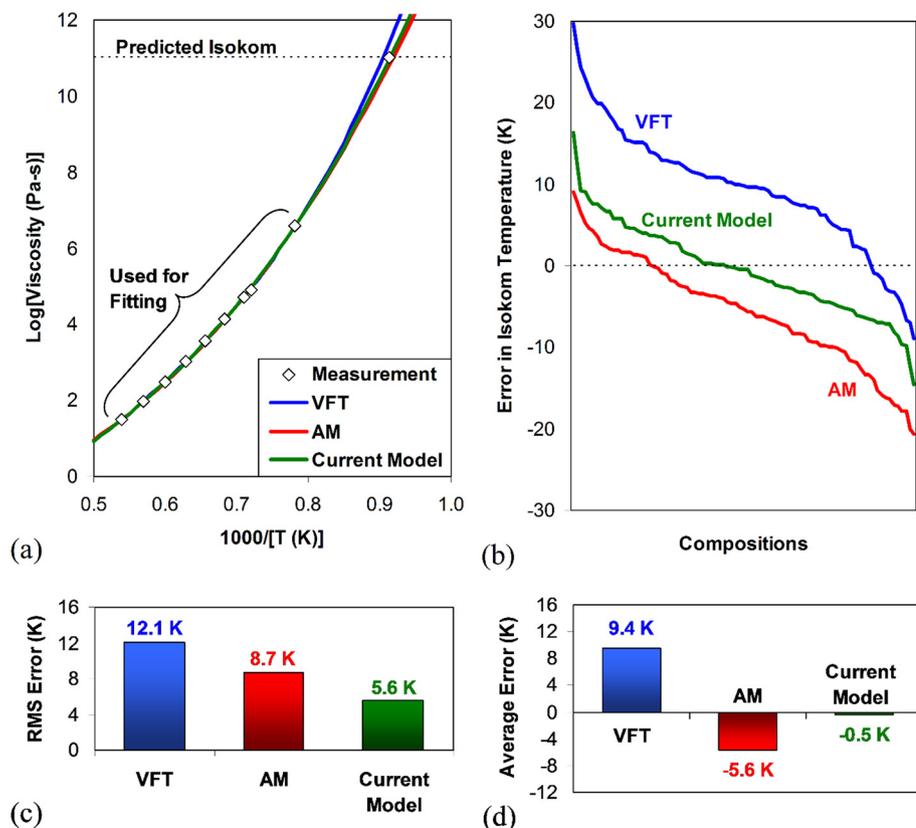


Fig. 5. Summary of results from the original MYEGA paper [71] published in 2009. (a) Low temperature extrapolation test, where the viscosity models are fit to high temperature viscosity data and then extrapolated to predict the 10^{11} Pa-s isokom temperature. (Here, "Current Model" refers to the MYEGA model.) (b) Error in the predicted 10^{11} Pa-s isokom for 85 different silicate compositions. The compositions on the horizontal axis are ordered in terms of descending error for the three models. (c) Root mean square error in the predicted isokom temperature using the three models. (d) Average error in the predicted isokom temperature. Modified from Mauro et al. [71].

basin follows a Boltzmann distribution over the restricted ensemble of the metabasin. The macroscopic properties of the glass-forming system can be calculated on any time scale using an appropriate weighted average over the basins.

Using the above metabasin partitioning process, the time step of the simulation scales proportionally with the experimentally relevant time scale. Hence, glass transition and relaxation behavior can be calculated on any arbitrary time scale, providing a versatile approach for calculating the long-time dynamics of glassy systems [62–64].

3.6. Configurational entropy of glass

The broken ergodic nature of glass also has important implications for its configurational entropy, a topic that has been the subject of intense study by Prabhat Gupta and coworkers over the past > 10 years [65–66]. In the traditional view, glass has a non-zero "residual entropy" at absolute zero temperature, a violation of the Third Law of Thermodynamics. This traditional view was usually justified by arguing that the Third Law applies only to perfect crystals and not to the disordered glassy state. However, the calculation of a non-zero residual entropy is based on an erroneous assumption of ergodicity in the glassy state. Prabhat's work has shown that the entropy of a glass is, in fact, zero at absolute zero temperature, and therefore glass does not require any special exception to the Third Law of Thermodynamics. The vanishing of entropy at absolute zero temperature is clear from Boltzmann's definition of entropy, $S = k_B \ln W$ where k_B is Boltzmann's constant and W is the number of microstates that yield a particular macrostate. At absolute zero all atomic motion has stopped, and the particular configuration of atoms in a glass must always be frozen, i.e., the macrostate of the glass is defined by just a single microstate, and the entropy is zero. The glass transition, therefore, involves a loss of configurational entropy as the breakdown of ergodicity occurs, and the liquid becomes frozen in a subset of the available energy landscape [65–66]. The formal proof of the zero entropy of glass at absolute zero was provided

by myself [67] based on fluctuation theory and the vanishing of heat capacity in the limit of absolute zero (indicating a vanishing of fluctuations and hence zero entropy).

3.7. Viscosity modeling

Viscosity is one of the most technologically important properties of glass-forming liquids. It has also presented a great scientific challenge, as the shear viscosity changes by over 12 orders of magnitude upon cooling from the initial glass melting regime through the glass transition range. Historically, the most successful equation for describing the temperature dependence of viscosity was the VFT equation, originally published in the 1920s [68]. The VFT equation was empirically proposed as a means of accurately capturing viscosity curves over many orders of magnitude, using only three fitting parameters. However, a fundamental problem with the VFT model is that it predicts a divergence of viscosity at finite temperature, leading to artificially high values of viscosity at low temperatures [69–70]. Also, since it is not physically derived, the VFT equation provides no means for predicting the composition dependence of viscosity.

In 2009, Prabhat was part of a team to propose the Mauro-Yue-Ellison-Gupta-Allan (MYEGA) equation, which provides a significantly improved description of the temperature dependence of supercooled liquid viscosity, especially at low temperatures [71]. The MYEGA equation was derived from Gupta-Mauro temperature-dependent constraint theory, assuming a two-state model representing the rigid-to-floppy transition. The MYEGA equation has the same number of adjustable parameters as the VFT equation, but it does not exhibit the same problem of finite temperature divergence and hence provides a significantly improved description of the temperature dependence of viscosity (see Fig. 5). Gupta-Mauro temperature-dependent constraint approach has also been used to extend the MYEGA equation to incorporate the composition dependence of viscosity [72]. Ten years after its introduction, the MYEGA equation is now the generally accepted

model for accurate descriptions of liquid and supercooled liquid viscosity.

While the MYEGA equation describes the viscosity of the liquid state, when the supercooled liquid is cooled through the glass transition, the structure becomes essentially frozen, and the viscosity of the glass departs from that of the liquid state at the same temperature [73]. This is the so-called “isostructural viscosity,” which has been a focus of Prabhat's research since his work on cathedral glass with Zanotto (see Section 2.4), which showed that the isostructural viscosity of glass can be many orders of magnitude lower than that of the corresponding liquid. More recently, Gupta and Heuer provided a detailed analysis of the general physics of isostructural viscosity in terms of the underlying energy landscape [74]. A recent review of viscosity modeling, including the temperature, composition, and thermal history dependence of viscosity—and Gupta's contributions to each of these important factors affecting viscosity—has recently been published by Zheng and Mauro [75].

4. Conclusions

It has been our pleasure to review several (but not all) of the great achievements of our dear friend and colleague, Prabhat Gupta. Prabhat serves as an excellent role model for young scientists, demonstrating the value of hard work, the importance of scientific rigor, and the ability to think creatively and challenge long-held assumptions and beliefs in the scientific community. Prabhat's impact of the field of glass science is indeed immense and will be felt for many decades to come. We hope that this brief review article has provided the reader with some sense of the tremendous impact of Prabhat's research. The remaining invited articles in this special issue of the *Journal of Non-Crystalline Solids X* will present some of the most recent advances in several of the areas that we have highlighted.

Interest statement

We declare no competing interests.

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