

Synopsis of the thesis entitled

**Study of Interatomic Interactions, Dynamics and
Thermodynamics in Transition Metals and its Alloys**

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By

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1. Introduction

The transition metals are widely used in the production of materials like metallic alloys and metallic glasses. The defining characteristics of metallic glasses, compared to conventional metallic materials, are their lack of crystallinity, and associated lack of macro-structural features such as phase and grain boundaries [1]. On account of the absence of crystal planes, metallic glasses possess very high physical strength (e.g., elastic modulus). These characteristics make the metallic glasses superior materials for corrosion- and wear-resistant coatings in luxurious products like laptop & mobile cases as well as for medical applications such as surgical blades, tooth and knee implants. Metallic glasses are also used to manufacture gears and other mechanical parts of miniature devices. Owing to the absence of magnetic domains, unlike crystalline alloys, these glasses exhibit very small hysteresis loss. So, the metallic glasses (in the form of ribbons or thin sheets) are widely used in high power transformer cores to reduce the hysteresis losses.

Metallic glasses are mainly obtained by rapid quenching of the melt with practically achievable rates as high as 10^7 K/s. During the liquid to glass transition, crystallisation of the melt is bypassed to yield a kinetically metastable liquid state i.e., supercooled liquid. The dynamics of the metallic-glass forming liquids exhibits a non-Arrhenius temperature dependence in the supercooled region below the melting temperature (T_m). The structural

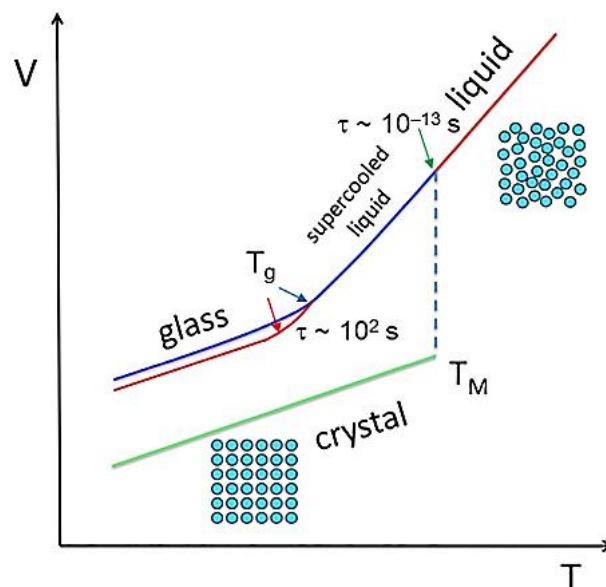


Figure 1: Schematic diagram demonstrating the change in thermodynamic variables during cooling of liquids and relevant timescales of atomic dynamics (ref. [2])

relaxation time, which is of the order of 10^{-12} s at T_m , rapidly increases. At temperature characterized as the glass transition temperature (T_g), it diverges to an extremely large value compared to the timescale for experimental measurements. (Fig. 1) The translation degrees of freedom of the atomic motion are nearly frozen at T_g and the liquid solidifies into the amorphous state. Thus, the dynamics of metallic liquids above T_m would have a significant bearing on the process of glass formation and the properties of the glasses produced by rapid quenching. Therefore, theoretical and experimental investigation of interatomic interactions, dynamics and thermodynamics in transition metals and their alloys are important to provide a better understanding of the dynamic, thermodynamic properties and its correlation with the glass-forming ability (GFA) of metallic glass-forming liquids.

The objectives of the research work to be presented in the thesis are as follows:

- To understand the interatomic interactions in transition metals and free energy of mixing in the transition metal alloys using pseudopotential formalism.
- To investigate the existing theories for the Brownian description of the single-particle dynamics and the dynamical correlations (specifically velocity autocorrelation function) in simple liquids and liquid metals.
- To investigate the correlation between the structural, thermodynamic properties and the GFA of Zr-based binary and ternary alloys.
- To study the influence of the doping of a rare earth (RE) element on the driving force for crystallization (Gibbs free energy difference between supercooled liquid and corresponding crystal state) and the GFA of Zr-based metallic alloys.
- Experimental investigation of the crystallization kinetics of heavy metal-based fluoride based ZBLAN glass using differential scanning calorimetry (DSC)

2. Organization of the Thesis

A detailed overview of the process of glass-formation in metallic glasses and the importance of the transition metals in the production of bulk metallic glasses and its applications will be given in *Chapter 1*. The motivation and objectives of the research work undertaken and, the statements of the investigated problems will be clearly described in this chapter.

Chapter 2 will focus on the study of the free energy of mixing in binary liquid alloys of transition metals. The theoretical framework [3] involves the modelling of the interatomic interactions and the effective pair potentials in pseudopotential formalism. The Wills and

Harrison (WH) approach [4], proposed specifically for the transition models, has been utilized to derive the effective pair potentials. The WH potential consists of three distinct contributions: (i) an s -electron like term; (ii) an attractive potential proportional to the d -band width; and (iii) a repulsive potential arising from the shift of the centre of gravity of the d -band. The WH interatomic pair potential for liquid transition metals is given by:

$$V(r) = V_S(r) - \frac{28.1}{\pi} \left(\frac{12}{n_c}\right)^{1/2} Z_s \left(1 - \frac{Z_d}{10}\right) \frac{r_d^3}{r^5} + \frac{225}{\pi^2} Z_d \frac{r_d^6}{r^8} \quad (1)$$

Here, Z_d is the d -electron valence, r_d is the d -band radius and n_c is the coordination number and it is taken to be 12 for transition metals.

WH formulation has further been modified by Bretonnet and Silbert (BS) [5] for partial inclusion of the d -state effects. WH considered the effect of d -electrons separately while, BS model considers the combine effect of sd -hybridization which can be explained in terms of form factors. The expressions of the form factors for WH and BS models are given as Eqs. (2) and (3) respectively.

$$W(q) = -\frac{4\pi z e^2}{q^2 \Omega} \cos(qr_c) \quad (2)$$

$$W(q) = 4\pi \frac{N}{V} a^3 \left[\frac{B_1 J_1}{(1+a^2 q^2)^2} + \frac{8B_2 J_2}{(1+4a^2 q^2)^2} \right] - \frac{4\pi Z_s e^2}{q^2} \frac{N}{V} \text{COS}(qR_c) \quad (3)$$

The detailed theoretical framework will be described in this Chapter. Illustrative results of the effective potentials for Cu and Fe modelled using the WH formulation are shown in Fig. 2.

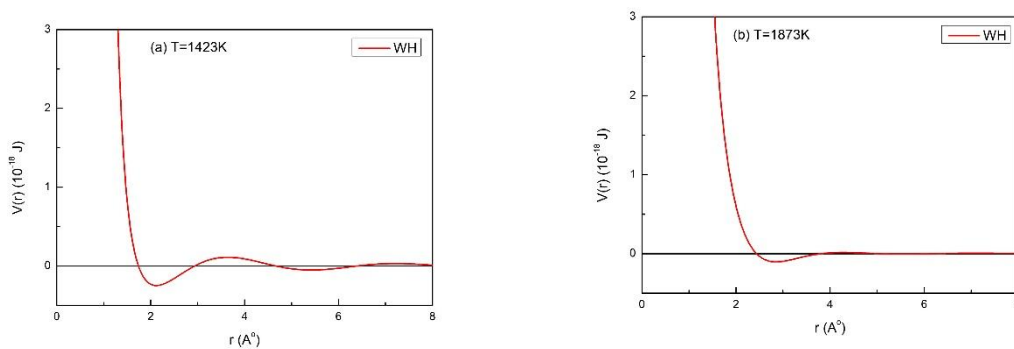


Figure 2 : Effective pair potentials for (a) Cu and (b) Fe obtained using the WH formulation

Chapter 3 of the thesis presents the study of single-particle dynamics in simple liquids and the liquid metals has been carried out in terms of the velocity autocorrelation function (VAF).[6] A microscopic theory of molecular motion in classical monatomic liquids, proposed by Glass and Rice [7], is revisited and extended to incorporate the dynamic friction in the

Brownian description of the atomic diffusion in a mean-time-dependent harmonic force field. A modified, non-Markovian Langevin equation is utilized to derive an equation of motion for the velocity autocorrelation function with time-dependent friction coefficient. The major highlight of the work is the consideration of the time-dependent friction in Brownian description of atomic motion in liquids and the derivation of the equation of motion

$$\frac{d^2\psi}{dt^2} + (\alpha + \beta_0 e^{-\alpha t}) \frac{d\psi}{dt} + \omega_0^2 e^{-\alpha t} \psi = 0 \quad (4)$$

Further detailed theoretical treatment will be described in the Chapter. Numerical solution of the equation gives an excellent account of the velocity autocorrelation function in LJ liquids, liquid alkali and transition metals over a broad range of density and temperature. Derivation of the equation of motion leads to a self-consistent expression for the time-dependence of friction coefficient. Our results demonstrate that the nature of time-dependence of the friction coefficient changes dramatically with the liquid density. At low and moderate densities, the dynamic friction decays exponentially whereas it increases exponentially at high liquid densities. Our findings provide an opportunity to have a new outlook of the Brownian description of atomic dynamics in liquids. Representative results are shown in Fig. 3.

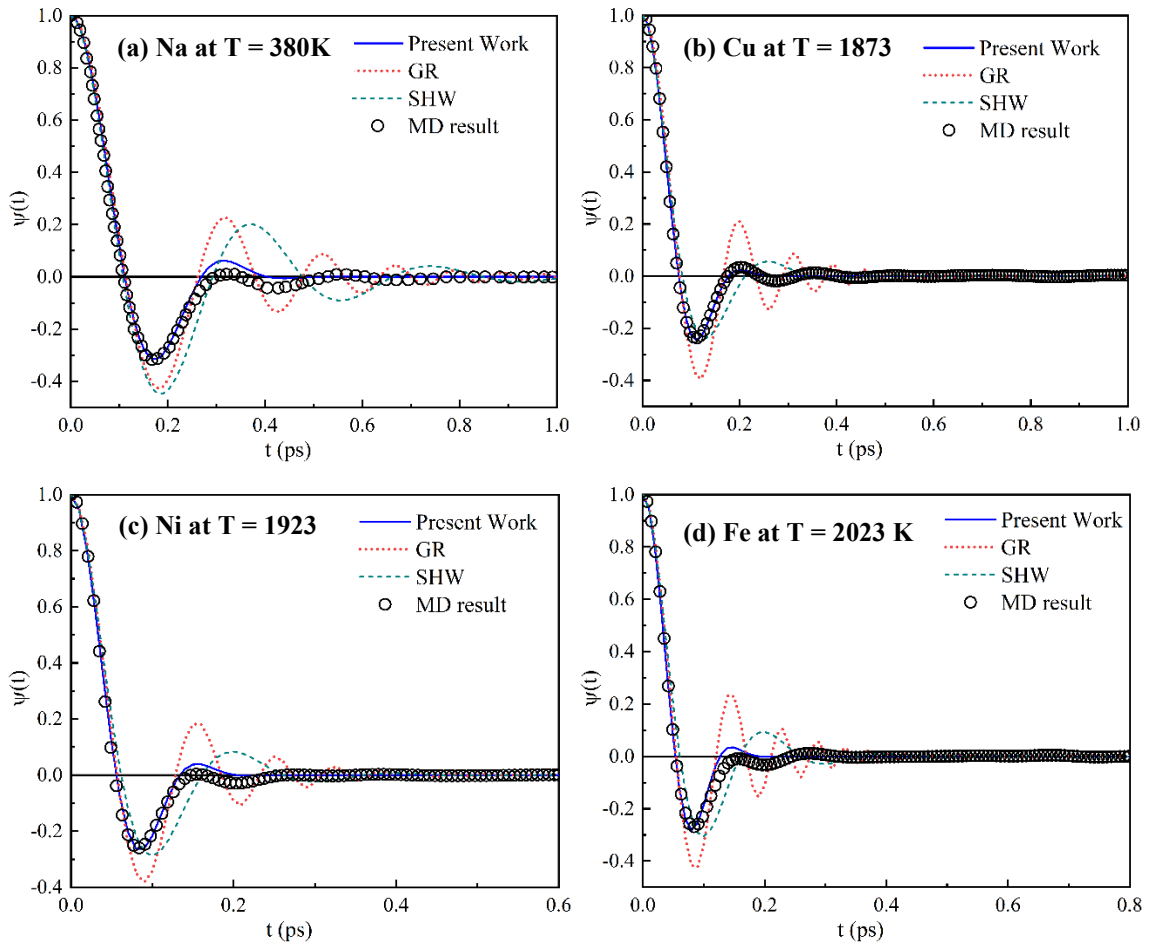


Figure 3 : Velocity autocorrelation function for the liquid metals, (a) Na, (b) Cu, (c) Ni and, (d) Fe

Bulk glass formation in multicomponent metallic liquids is a complex process that is governed by several inter-related factors such as the topological and chemical short-range order, thermodynamic drive force, enthalpy of mixing etc. Inoue [8], proposed three empirical rules to predict better GFA. These rules mainly involve three factors namely, the number of elements in the alloys, atomic size mismatch and heat of mixing. It suggests that three or more elements with atomic size mismatch $> 12\%$ and negative heat of mixing between the main elements should be a prerequisite for an alloy to be a good glass former. These factors are most often interrelated and govern the thermodynamic behaviour as well as the stability of the alloys against crystallization in the supercooled region. As the GFA of these alloys depends on its composition, it is a challenging task to identify the compositions with high GFA. *Chapter 4* of the thesis presents the study of the effect of topological packing on the excess entropy, the configurational entropy, and the mismatch entropy in Cu-Zr and Cu-Zr-Al alloys have been investigated using an analytical approach based on the equation of state for the mixture of hard spheres. [9]

The essential input parameter for this approach, the atomic packing fraction (η), has been derived from the classical MD simulations and subsequent analysis of 3D atomic level structure. As we have used composition dependent η , our results for the different entropic terms are much more realistic compared to similar studies on binary and ternary alloys where η is uniformly assumed to be equal to 0.64 for all the alloy compositions. The mismatch entropy and the change in the excess entropy of mixing show good correlation with the GFA in Cu-Zr alloy in a wide composition range. It suggests that the analytical approach based on hard sphere mixture model is appropriate for the description of the thermodynamic properties of Cu-Zr alloys. For Cu-Zr-Al alloys, however, this approach is effectively applicable in the limited composition range with Al < 10% due to dominant chemical-short range ordering on account of increasing Al%. The composition dependence of the different entropic terms for both binary and ternary alloys, in general, indicates that the contributions of all the entropy terms to the total entropy should be maximum for better GFA. It is consistent with the entropy maximization in process of glass formation. Fig. 4 shows the representative results for the studied Cu-Zr and Cu-Zr-Al alloys.

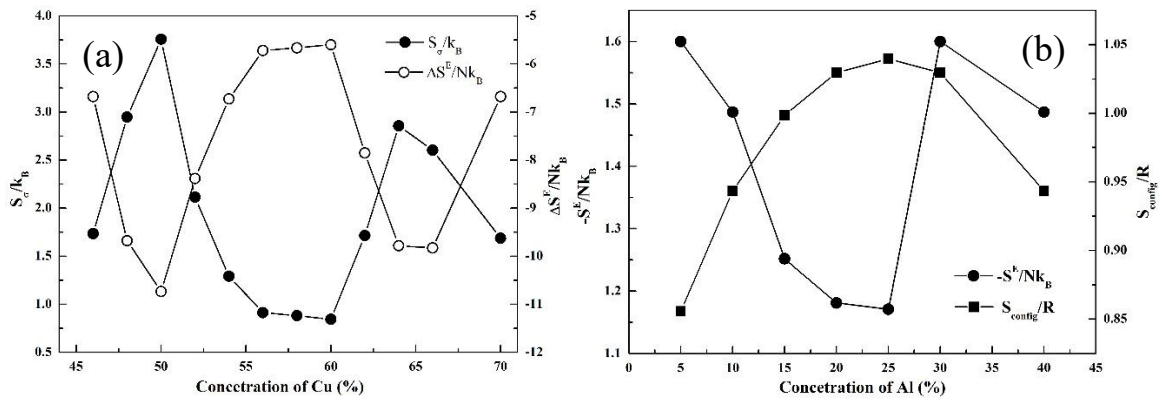


Figure 4 : (a) Mismatch entropy and the change in the excess entropy in $\text{Cu}_x\text{Zr}_{100-x}$ alloys
(b) Compositional dependence of Excess entropy and configurational entropy in $\text{Cu}_{50}\text{Zr}_{100-x}\text{Al}_x$ alloys.

Chapter 5 of the thesis presents the theoretical investigations on the estimation of the Gibbs free energy difference (ΔG) between the supercooled liquid and the corresponding crystalline state of the multicomponent Zr-based metallic glass-forming liquids. ΔG is an important parameter in nucleation processes. The nucleation frequency has an exponential dependence on ΔG , and hence its estimation is often critically important when used in the analysis of nucleation phenomena. [10] It is well-known fact that the mixing of solute the atoms of the host element leads to the formation of local atomic clusters with five-fold symmetry

which is incompatible with the three-dimensional packing. The resultant geometrical frustration promotes glass formation in an alloy. However, the presence of impurity atoms such as carbon, oxygen etc. adversely affects the GFA of an alloy. In case of mixing of rare-earth/transition metal elements, a large amount of charge transfer occurs due to the difference in their electronegativity. The doping of rare-earth elements also helps to remove the impurities to yield better GFA [11]. Therefore, the concentration of rare-earth elements in transition metal-based multicomponent alloy plays a dominant role in controlling the fundamental factors like the atomic packing and heat of mixing that affect GFA. In the present work, the effect of yttrium (Y) doping on the thermodynamics of the $Zr_{56-x}Co_{28}Al_{16}Y_x$ ($x = 0, 2, 7, 10$ at. %) alloys in the supercooled region and GFA. [12]. Thermodynamic behaviour of these alloys has been studied using an analytical approach where some of the key thermodynamic quantities such as ΔH , ΔS and ΔG have been estimated using a hyperbolic temperature dependence of specific heat difference ΔC_p in the supercooled liquid region. The analytical approach has been found to give estimates of ΔG in a wide supercooled liquid region which is in excellent agreement with the experimental results. Estimated ΔG values are found to be minimum for Y concentration of 7% and 10% which is consistent with the observed high GFA for these compositions. (Fig. 5) Fundamental elemental properties such as atomic size, electronegativity, the heat of mixing have been found to play an important role in governing the thermodynamics of the alloys in the supercooled liquid region.

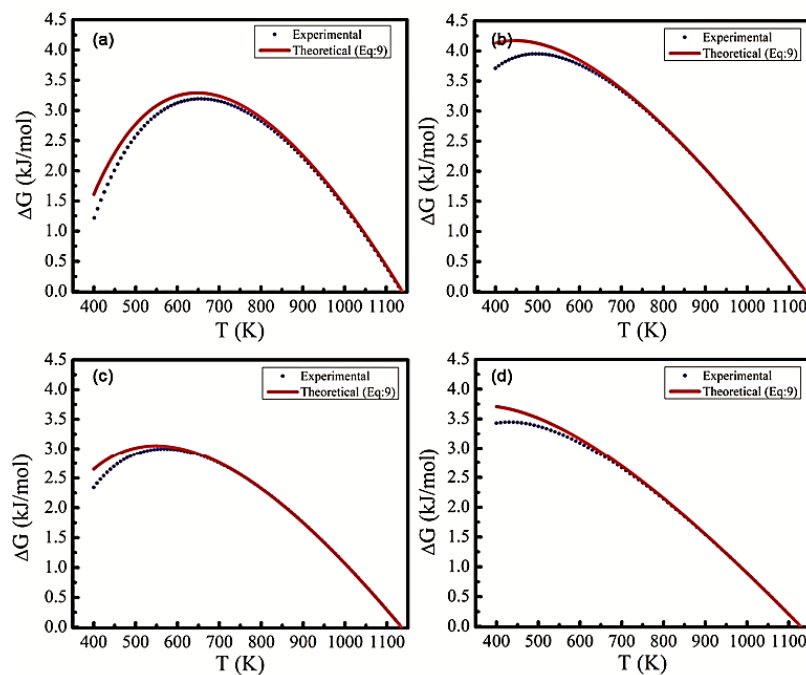


Figure 5 : Gibbs free energy difference ΔG for (a) $Zr_{56}Co_{28}Al_{16}Y_0$, (b) $Zr_{54}Co_{28}Al_{16}Y_2$, (c) $Zr_{49}Co_{28}Al_{16}Y_7$ and (d) $Zr_{46}Co_{28}Al_{16}Y_{10}$

Chapter 5 also include the experimental investigations on a commercially important heavy metal fluoride glass known as ZBLAN. It possesses high thermal stability and excellent property as a transmitting material. [13] The current study examines the thermal properties of ZBLAN glass utilizing Differential scanning calorimetry (DSC) at various heating rates. The glass transition temperature, T_g , is observed to vary with heating rate, indicating its kinetic nature. Through the use of Kissinger [14] and Augis-Bennett methods [15] and the heating rate dependence of T_g , the activation energy (E) has been determined. These methods have also been used to obtain the fragility index (m), which can be used to evaluate the glass forming ability (GFA) of the system. The fragility index found is greater than 16, indicating that the ZBLAN glass is "fragile." [16] The representative results of the DSC thermogram and the Kissinger plot are shown in Fig. 6.

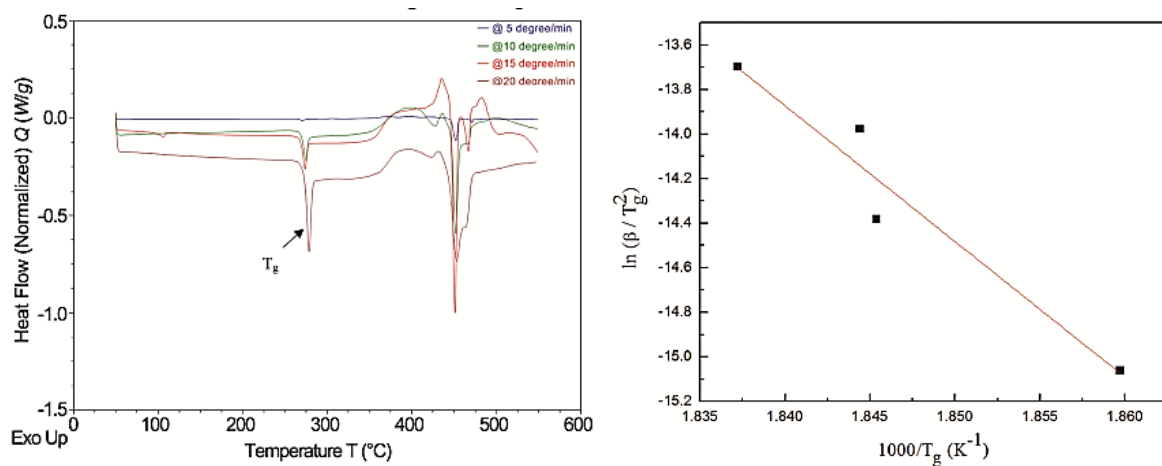


Figure 6 : (a) DSC thermograms of ZBLAN Glass at four different heating rates, (b) Kissinger plot

Finally, important conclusions drawn out the investigations presented in the thesis will be summarized in *Chapter 6*. Also, the possible extensions of the present work will be discussed as future scope for further work.

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List of Publications

Papers published in peer reviewed Journals

1. **Margi K. Patel**, Deepak Upadhyay, Kirit N. Lad & Arun Pratap, “Yttrium Enhanced Glass-Forming Ability of Zr-Based Metallic Glasses”, **Indian Journal of Pure & Applied Physics** **59** (2021) 803-810.
2. Kirit N. Lad, **Margi K. Patel**, Arun Pratap, “Brownian motion with time-dependent friction and single-particle dynamics in liquids”, **Physical Review E.** **105** (2022) 064107.
3. **Margi K. Patel**, Chintan D. Parmar, Naveen Acharya, Arun Pratap. “Experimental investigation of kinetics of glass transition of ZBLAN glass by using differential scanning calorimetry” **Indian Journal of Pure & Applied Physics** **61** (2023) 15.

Papers in Conference Proceedings

1. **Margi K. Patel**, Irfan Malek, Mit C. Shah, Kirit N. Lad, Arun Pratap, “Correlation between Entropy and Glass-forming Ability in Cu-Zr and Cu-Zr-Al alloys” **Materials Today: Proceedings.** **47** (2021) 587.

Conferences/Seminars/Workshops

2018: (1) Workshop on Numerical Methods and Computer Programming (NMCP),

August, 06-10, 2018, UGC DAE, Consortium for Scientific Research, Indore,

India

- (2) National Research Scholar Meet on Condensed Matter Physics and Material Science (CMPMS-18), December 08, 2018, Department of Physics, Gujarat University, Ahmedabad, India.

Poster Presentation: Study of Atomic Dynamics in Liquid Transition Metals using Brownian Description

- 2020: (1) Webinar on Art of Writing Research Paper, May 29, 2020, Department of Computer Science and Engineering, University School of Information and Communication, Gautam Buddha University, Greater Noida, Uttar Pradesh, India.

- (2) Online Quiz – Physics 2020, June 06, 2020, Self-Finance College, Dabhoi, Gujarat, India.

- (3) Webinar on Century of Quantum Mechanics and Still Going Strong, June 15-17, 2020, jointly organized by Applied Physics Department (Faculty of Tech. & Engg. The M. S. University of Baroda), Gujarat Science Academy (GSA), Indian Physics Association (IPA) Baroda Chapter and Indian Association of Physics Teachers (IAPT-RC7) in association with National Academy of Sciences, India (NASI) Delhi Chapter.

- (4) National Conference on Recent Advancements in Materials Science and Nanotechnology (RAMAN)-2020, July 30-August 01, 2020, Department of Electronics and Communication Engineering, Nirma University, Ahmedabad, Gujarat, India.

Paper Presentation: Correlation between Entropy and Glass-forming Ability in Cu-Zr and Cu-Zr-Al alloys.

- 2021: (1) International Symposium on Applications of Thermal Analysis and Calorimetry (SATAC-2021), December 21-22, 2021, University department of Chemistry, Magadh University, Bodh Gaya, India.

Paper Presentation: Crystallization Kinetics of ZBLAN glass.