



# Structural aspects of the Stokes-Einstein relation breakdown in high temperature melts



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## ABSTRACT

Dynamical and structural properties of four Al-Fe melts ( $\text{Al}_{100-x}\text{Fe}_x$ ,  $x = 10, 20, 30$ , and  $40$ ) were calculated using molecular dynamics simulation over a wide temperature range. The dynamical results reveal that, a crossover from Arrhenius to non-Arrhenius behavior occurs for  $\alpha$ -relaxation time  $\tau_\alpha$  and shear viscosity  $\eta$  bordered at  $T_x \sim 1.2T_L$  ( $T_L$  the liquidus temperature). At  $T_x$ , we also found the breakdown of Stokes-Einstein relation and the rapid enhancement of dynamic heterogeneity. The structural results demonstrate that the fraction of icosahedral cluster increases with decreasing temperature, and the amplitude of increase has a significant shift at  $T_x$ . In order to facilitate a uniform description, local five-fold symmetry (LFFS) was selected to describe the development of various kinds of atomic clusters. It is seen that LFFS has an obvious change at  $T_x$ , implying a strong coupling between atomic dynamics, SER breakdown and liquid structure change. For the first time, the breakdown of SER is demonstrated to have a structure signature which could be characterized by LFFS. This work would be helpful in understanding the longstanding challenges of the dynamics-structure relationship in liquid metals.

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## 1. Introduction

Dynamical properties of liquid metal, such as self-diffusion coefficient ( $D$ ) and viscosity ( $\eta$ ), play a crucial role in nucleation, crystal growth and glass transition [1,2]. The determination of  $D$  and  $\eta$  is of great significance both theoretically and practically. However, a precise measurement of  $D$  and  $\eta$  is very sparse due to the experimental difficulties. In the absence of available experimental data, it is an alternative way to approximate  $D$  from  $\eta$  or vice versa using the well-known Stokes-Einstein relation (SER) [3,4]:

$$D = k_b T / (cd\eta), \quad (1)$$

where  $k_b = 1.38 \times 10^{-23}$  J/K is the Boltzmann constant,  $T$  the absolute temperature,  $d$  the effective particle diameter, and  $c$  a constant depending on boundary conditions:  $3\pi$  for stick boundary condition and  $2\pi$  for slip boundary condition. The slip boundary condition seems more suitable for metallic melts, and has been widely utilized by researchers [5–8].

SER was originally established to describe the diffusive motion of a mesoscopic sphere in a viscous medium [9,10]. But it is astonishingly observed that in many liquids SER works quite well over a broad temperature range as a phenomenological theory [11–13]. Generally, SER can reasonably describe the relationship between  $D$  and  $\eta$  at sufficient

high temperatures. As temperature decreases to a critical value of  $T_c$ ,  $D$  will decouple from  $\eta$  (i.e., SER breaks down). According to the mode coupling theory (MCT), the critical temperature  $T_c$  characterizes a change for atomic motion from the ergodic liquid-like viscous flow to non-ergodic solid-like hopping [14].  $T_c$  is experimentally found to fall in between  $T_g$  and  $T_L$  ( $T_g$  the caloric glass transition temperature and  $T_L$  the liquidus temperature) [15]. However, with the development of experimental techniques, many studies reveal that SER already breaks down at the temperature of  $T_x$  which is far above  $T_c$  and even above  $T_L$ . It is reported in a Zr-Ti-Cu-Ni-Be melt that  $D$  of Ni and Ti decouples from  $\eta$  at  $T$  far above  $T_c$  [16]. Using the advanced electrostatic levitation, Brillo et al. found  $D_{(\text{Ni})}\eta$  is temperature independent in  $\text{Zr}_{64}\text{Ni}_{36}$  liquid over a temperature range of 800 K [17]. And it should be emphasized that  $D_{(\text{Ni})}\eta = \text{const.}$  is found to hold at  $T$  above  $T_L$  by about 500 K. This finding is contradicting with the prediction of SER and cannot be explained by MCT, which is a strong indication that we still have much to do in characterizing atomic dynamics in liquid metals.

An investigation of the SER breakdown not only is crucial in understanding the dynamic slowing down, but also has a high value in practical applications. Consequently, the breakdown of SER is a research focus in condensed matter physics. Up to now, the breakdown of SER at  $T > T_c$  has been reported in many different liquid systems, such as Zr-Ti-Cu-Ni-Be [16], Ni-Zr [17], Cu-Zr [18,19], Al-Ni [20], and Cu-Zr-Al [21], indicating that it may be a widely-existed event. However, despite the intensive studies, several questions still remain elusive such as what is the possible underlying mechanism for this high temperature breakdown, does this breakdown has a universal signature, is there a convenient

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method to predict such a high temperature breakdown, and so forth. Those questions closely associate with each other and right now discussed controversially.

Recently, we found the high temperature breakdown of SER in  $\text{CuZr}_2$  [18] and  $\text{Cu}_8\text{Zr}_3$  [19] melts, this breakdown occurs at  $T_x$  which is far above  $T_c$  and even above  $T_l$ . We ascribed this breakdown to the sudden increase of dynamics heterogeneity (DH) in the melts. Further, the parameter  $d(D_1/D_2)/dT$  was demonstrated as a useful indicator to predict  $T_x$ , where  $D_1/D_2$  is the ratio of self-diffusion coefficients of the two components. At the same time, we pointed out that  $d(D_1/D_2)/dT$  may be highly influenced by composition and chemical bond. A systematic work is needed to elucidate whether  $d(D_1/D_2)/dT$  could be used to characterize the high temperature breakdown of SER in other systems. There exists another problem that,  $d(D_1/D_2)/dT$  is confined to binary or multi-component systems and cannot be applied to monatomic systems. So  $d(D_1/D_2)/dT$  is not a universal signature to predict  $T_x$ , a more general one is needed.

At present it becomes a common belief that dynamics is connected to local structure in liquids, and many dynamic behaviors have a structural origin [22–27]. Kawasaki et al. demonstrated in a glass forming colloidal liquids that both dynamics slowing down and DH are intrinsically correlated with liquid structure [23–25]. Zheng et al. suggested that an increase in the size of the glassy cluster can lead to the dynamics slowing down in monolayers of colloidal ellipsoids [26]. Xia et al. even indicated that the glass transition has a structure origin in a hard-sphere system [27]. Considering those studies together, it concludes that there may be a universal correlation between dynamics and structure. It is also worth noting that, the high temperature breakdown of SER is verified to strongly couple with liquid structure change in Cu-Zr [19], Al-Ni [20] and Cu-Zr-Al [21] melts. If we want to find a universal signature of the SER breakdown, it seems liquid structure is a good research point.

Therefore in this work we try to explore a possible universal signature from the view of liquid structure. This structure signature should be equally applied to various liquid systems. We carried out molecular dynamics (MD) simulation with a well-accepted embedded atom method potential. Al-Fe alloy was adopted as the prototype system. The reasons are as follows: Firstly, Al-Fe alloys possess attractive properties making them very interesting for engineering applications [28, 29]. The calculated dynamic data are very useful to the computer-aided analysis and prototyping in casting industry. Secondly, Al-Fe-based alloys with Al content up to 90 at% are the potential metallic glass forming systems [30–32], knowledge of dynamic slowing down for such a system is helpful to uncover glass transition mechanism. Thirdly, different from Cu-Zr pair, Al-Fe pair is a strong chemical bond. We can test whether the previously proposed parameter  $d(D_1/D_2)/dT$  is still useful or not in this strong bonding system.

## 2. Computational methods

The MD simulations were carried out for Al-Fe systems of  $N = 32,000$  atoms using the open source parallel simulator LAMMPS [33]. The cubic simulation boxes were subject to periodic boundary conditions in three directions. The velocity Verlet algorithm with a time step of 1 fs was employed to solve the motion equation at isothermal-isobaric ensemble (NPT). The temperature was controlled by the Nose-Hoover method [34] and zero pressure was kept using the Parrinello-Rahman algorithm [35]. The atomic interaction was modeled by a Finnis-Sinclair type potential which was developed by Mendev et al. [36]. The initial configuration was established according to the stoichiometric ratio (including  $\text{Al}_{90}\text{Fe}_{10}$ ,  $\text{Al}_{80}\text{Fe}_{20}$ ,  $\text{Al}_{70}\text{Fe}_{30}$ , and  $\text{Al}_{60}\text{Fe}_{40}$ ). Liquid Al-Fe alloys were first equilibrated at 2550 K (well above the melting point of alloys) for 600 ps. Then the equilibrated liquids were quenched to 50 K at the cooling rate of  $10^{12}$  K/s. The energy and density profiles during the cooling are shown in Supplementary Fig. S1. At each considered temperature, the recorded configurations were additionally equilibrated for 30 ps. During the equilibrated process, no aging effects were

observed. Then the equilibrated configurations were used to calculate the expected properties.

Self-diffusion coefficient  $D$  is derived from the long time evolution of mean-square displacements (MSDs),

$$\langle r^2(t) \rangle = \frac{1}{N} \sum_{i=1}^N [r_i(t) - r_i(0)]^2, \quad (2)$$

using the Einstein equation

$$D = \lim_{t \rightarrow \infty} \frac{1}{6t} \langle r^2(t) \rangle, \quad (3)$$

where  $\langle \dots \rangle$  denotes the ensemble average.  $\alpha$ -relaxation time  $\tau_\alpha$  is defined as the time needed for the self-intermediate scattering function  $F_s(q, t)$  to decay to  $e^{-1}$ :

$$F_s(q, t) = \frac{1}{N} \left\langle \sum_{j=1}^N \exp\{-iq \cdot [r_j(t) - r_j(0)]\} \right\rangle, \quad (4)$$

where  $N$  is the atom number,  $r_j$  the position of atom  $j$ , and  $q$  the wave vector corresponding to the first peak position of static structure factor. As an example, supplementary Fig. S2 gives the typical behavior of MSD and  $F_s(q, t)$  as a function of time at different temperatures, from which  $D$  and  $\tau_\alpha$  can be well determined.  $\eta$  is calculated by the time integral over the pressure autocorrelation function (as shown in Supplementary Fig. S3) using the Green-Kubo relation [37]

$$\eta = \frac{V}{k_b T} \int_0^\infty \left\langle \sum_{\alpha \neq \beta} P_{\alpha\beta}(t) P_{\alpha\beta}(0) \right\rangle dt, \quad (5)$$

where  $P_{\alpha\beta}(t)$  is the off-diagonal element ( $\alpha \neq \beta$ ,  $\alpha, \beta = x, y, z$ ) of the pressure tensor at time  $t$ ,  $V$  the volume of system, and  $k_b$  the Boltzmann constant. To guarantee the consistency and repeatability of data, each calculation process was repeated three times.

## 3. Results and discussion

### 3.1. Static structure factor $S(q)$ and pair correlation function $g(r)$

Static structure factor  $S(q)$  is a widely-used quantity to characterize liquid structure in the reciprocal space, which can be well measured by neutrons or X-rays scattering experiments. So far,  $S(q)$  of Al-Fe liquid alloys has been well detected by experiments [38]. At first, we routinely gave the present simulated  $S(q)$  along with the X-rays diffraction data [39,40] in Fig. 1. As we can see, there is an overall agreement between

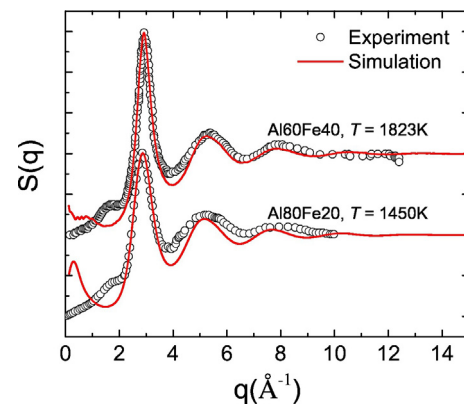


Fig. 1. A comparison between simulated and experimental static structure factors  $S(q)$ s for  $\text{Al}_{80}\text{Fe}_{20}$  melt at  $T = 1450$  K and for  $\text{Al}_{60}\text{Fe}_{40}$  melt at  $T = 1823$  K. The experimental data for  $\text{Al}_{80}\text{Fe}_{20}$  and  $\text{Al}_{60}\text{Fe}_{40}$  melts are from Refs [39,40], respectively.

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