Elementary Excitations and Crossover Phenomenon in Liquids

T. Iwashita, D. M. Nicholson, and T. Egami

Phys. Rev. Lett. **110**, 205504 — Published 16 May 2013

DOI: 10.1103/PhysRevLett.110.205504

Elementary excitations and crossover phenomenon in liquids

T. Iwashita[1], D. M. Nicholson[2] and T. Egami[1,2,3]

[1]*Joint Institute for Neutron Sciences and Department of Physics and Astronomy, University of Tennessee, Knoxville, TN 37996*

[2]*Oak Ridge National Laboratory, Oak Ridge, TN 37831*

[3]*Department of Materials Science and Engineering, University of Tennessee, Knoxville, TN 37996 USA*

Abstract

The elementary excitations of vibration in solids are phonons. But in liquids phonons are extremely short-lived and marginalized. In this letter through classical and *ab-initio* molecular dynamics simulations of the liquid state of various metallic systems we show that different excitations, the local configurational excitations in the atomic connectivity network, are the elementary excitations in high temperature metallic liquids. We also demonstrate that the competition between the configurational excitations and phonons determines the so-called crossover phenomenon in liquids. These discoveries open the way to the explanation of various complex phenomena in liquids, such as fragility and the rapid increase in viscosity toward the glass transition, in terms of these excitations.

PACS#:

The physics of phonon in crystalline solids is well-understood [1]. For instance its frequency can be calculated by diagonalizing the dynamical (Hessian) matrix, the matrix of which elements are the second derivative of the total energy with respect to the atomic displacements [1]. In liquids, however, the dynamical matrix itself is time-dependent because the atomic structure is changing with time. If the dynamical matrix varies as fast as, or faster than phonons [2] the validity of the concept of phonon becomes questionable. Yet, it is known that at high temperatures the specific heat of a liquid approximately satisfies the Dulong-Petit law of $C_V = 3k_B$ [3], suggesting the presence of some well-defined excitations. But the nature of such excitations in liquids is unknown. In general we know very little about the atomic dynamics in liquids. Theoretically the flow of a liquid is commonly described by continuum hydrodynamic theories [4, 5]. Less attention has been paid to the atomic level dynamics because it has been believed that the liquids were so random that details of the atomic motion were irrelevant to the physics of liquid flow. For instance the energy landscape theory describes atoms in a liquid at high temperatures as diffusing almost freely well above the peaks and valleys of energy landscape, seeing only shallow minima [6]. Actually at high temperatures above the so-called crossover temperature viscosity shows the Arrhenius behavior of thermal activation [7, 8]. However the nature of such activation processes and the origin of the crossover behavior remain unclear.

In this letter we show that elementary excitations different from phonons exist in liquids, and they are the origin of viscosity, and that the competition between the high temperature elementary excitations and phonons results in the crossover phenomenon in liquids. This is done through classical as well as *ab-initio* molecular dynamics (MD) simulations on various metallic liquids in either NVT or NPT ensembles. The periodic boundary condition on a cubic box was imposed for all systems. For liquid iron the model consisted of 16,384 atoms interacting via the modified Johnson potential [9]. The binary Kob-Andersen (KA) model [10] of 80/20 mixture (80% particle *A* and 20% particle *B*) consisted of 10,976 Lennard-Jones (LJ) particles at a reduced density of 1.2. All results for KA model are expressed in argon units. The simulations were performed in a temperature range from 60K to 300K, under NVT ensemble. For $Cu_{56}Zr_{44}$ and $Zr_{50}Cu_{40}Al_{10}$, we employed embedded atom method (EAM) potentials [11, 12] and simulated the systems with 16,000 atoms for $Cu_{56}Zr_{44}$ under NVT ensemble, and with 32,000 atoms for $Zr_{50}Cu_{40}Al_{10}$ under NPT ensemble with pressure equal to zero. The simulations were carried out using the LAMMPS software. *Ab initio* MD simulations of $Cu_{56}Zr_{44}$ in the NVT ensemble were performed using dynamics based on forces from the Projector Augmented-Wave (PAW) method [13] (Gamma point only) as implemented in the VASP 4.6 code [14]. The simulation cell contained 200 atoms with periodic boundary conditions. The sample was equilibrated using a Nosé-Hoover thermostat [15, 16] at T = 4000, 4500 and 5000K for 3 ps followed by 1.1 ps of data collection during which the positions and stress matrix were recorded every time step (fs). Further details of the methods are given in Supplemental Material.

The viscosity, η, is a key parameter describing the dynamics of liquids. It is given by the Green-Kubo formula [17],

$$\eta = \frac{V}{k_B T} \int_0^{\infty} \langle \sigma^{xy}(0) \sigma^{xy}(t) \rangle dt \qquad (1)$$

where σ^{xy} is the *x-y* component of the stress tensor, T is the temperature and V is the volume of the liquid. The time-scale of liquid dynamics is determined by the Maxwell relaxation time τ_M,

$$\tau_M = \frac{\eta}{G_\infty} \ , \tag{2}$$

where

$$G_\infty = \frac{V}{k_B T} \langle \left(\sigma^{xy}(0)\right)^2 \rangle \tag{3}$$

is the high-frequency shear modulus [17]. If the time-scale of the experiment is shorter than τ_M the system behaves like a solid, whereas if it longer it behaves like a liquid. It has been suggested that τ_M is related to the α-relaxation time, τ_α [18], and the bond-lifetime, τ_B [19]. The α-relaxation time is determined from the intermediate scattering function at the first peak of the structure function, $S(Q)$ [17]. In the metallic systems under consideration here chemical bonds are not well-defined. However, it is possible to define the atomic connectivity network by defining the "bond" between the nearest neighbor atoms. This is because the nearest and the second nearest neighbors are well separated in the atomic pair-density function (PDF). We define the distinction between the 1st and 2nd nearest neighbors by the minimum in the PDF between the 1st and 2nd peaks.

In Figure 1 we compare the temperature dependences of τ_M, τ_α, and τ_B for liquid Fe. Indeed three relaxation times show similar temperature dependences, but they are different in magnitude. τ_α is longer than τ_M by a factor of about three, and τ_B is even longer, by an order of magnitude, than τ_α [19]. On the other hand the life-time of the state of local atomic connectivity, τ_{LC}, [20] is in much closer agreement with τ_M as shown also in Figure 1. Here τ_{LC} is defined as the time for an atom to lose or gain one nearest neighbor (Figure 2), thus changing the local atomic connectivity through local configurational excitation (LCE). In Figure 3 τ_M and τ_{LC} are shown in logarithmic scale against $1/T$ for various systems. Both show the Arrhenian behavior at high temperatures, but deviate from it below T_A, the crossover temperature. Figure 3 suggests that τ_M and τ_{LC} are similar in value above T_A for all systems.

It is interesting to note that in all liquids, other than the KA model which has a rather different energy scale, τ_M and τ_{LC} extrapolate to about $\tau_\infty = 20$ fs at the limit of $T \to \infty$ (Table 1). This value of τ_∞ corresponds to about 200 meV. The activation energy is also about 200 meV. These results are more consistent with the LCE's characterized by the bond energy (250 meV for Fe) than phonons (the Debye frequency is about 40 meV).

We show in Figure 4 the ratio, τ_M / τ_{LC}, as a function of T/T_A for various systems including the results of the *ab-initio* MD simulations. In spite of differences in composition and the method of MD this ratio, τ_M / τ_{LC}, is remarkably close to unity at temperatures above T_A. Given some small uncertainty in defining the nearest neighbors, as discussed in the Supplemental Material, the result strongly suggests that the relation,

$$\tau_M = \tau_{LC} \qquad (T > T_A), \tag{4}$$

is universally valid for metallic liquids at high temperatures. This is an important result, because this equation directly connects a macroscopic quantity, τ_M, with a microscopic quantity, τ_{LC}. In liquids phonons are strongly scattered, short-lived, and cannot be used as the basis to explain other properties such as viscosity which shows the Arrhenian behavior. Instead, this result suggests that LCE is the elementary excitation in the high-temperature liquid. LCE's are not long-living harmonic excitations as are phonons. However, they are the elementary steps to change the atomic connectivity network, and directly control the macroscopic viscosity. Thus it is likely that LCE's represent the full degrees of freedom in the liquid as elementary excitations, just as phonons do in solids.

From equations (1) - (3) we obtain [21],

$$\tau_M = \int_0^\infty \frac{\left\langle \sigma^{xy}(0)\sigma^{xy}(t)\right\rangle}{\left\langle \left(\sigma^{xy}(0)\right)^2\right\rangle} dt . \tag{5}$$

Therefore equation (4) means that the lifetime of the shear correlation function is determined by the lifetime of local atomic connectivity. This is reasonable because the macroscopic shear stress is a sum of the atomic-level shear stresses [22], and the atomic-level stress is determined largely by the topology of the nearest neighbors [23]. For instance the atomic-level pressure is linearly related to the local coordination number [24]. Thus LCE's are the elementary excitations for the atomic-level stresses. This explains why the equipartition theorem for atomic-level stresses [23] as well as the Dulong-Petit law [3] are valid for high-temperature liquids.

We find that the crossover phenomena at T_A are closely related to localization of phonons. The mean-free path of transverse phonon,

$$\xi_p = c_T \tau_M \tag{6}$$

where c_T (= $\sqrt{G_\infty/\rho_0}$, ρ_0 is the physical density) is the transverse sound velocity, decreases with increasing temperature. At high temperatures it is shorter than a, the distance between the nearest neighbors, and phonons are localized [25,26]. The temperature T_I, at which ξ_p becomes equal to a (see Supplemental Material), is shown by arrows in Figure 4, demonstrating that T_I is very close to T_A. Agreement between T_A and T_I is not perfect, but this may be partly because T_A is not so accurately defined due to the crossover nature of the phenomena. Interestingly in the case of KA glass we had to use the second neighbor *B-B* distance for a, because of the strong *A-B* chemical bond. Above T_A the lifetime of local atomic configuration is so short that the local atomic connectivity changes before atoms communicate with neighbors through atomic vibrations. Thus LCE's are independent of each other above T_A.

In the energy landscape picture, below the crossover temperature the system starts to sample deeper landscape minima, and enters the "landscape influenced" regime [3, 27]. A number of properties of liquid exhibit significant changes in their nature through T_A [6-8, 28, 29]. However, it had not been known what controlled the crossover point. The present result makes clear that the dynamic communication among atoms is the deciding factor, and the Ioffe-Regel localization [25] of transverse phonons into the LCE's is the physics behind this phenomenon.

Below T_A the ratio, τ_M / τ_{LC}, increases with decreasing temperature. Because the local atomic connectivity is closely related to the atomic level stresses, an LCE, the action of breaking or creating a bond, will change the atomic level stresses of the two atoms involved in the broken or created bond. At $T > T_A$ τ_{LC} is too short for LCE to affect neighboring atoms other than the two involved in the bond, but at low temperatures τ_{LC} is long enough for LCE's to create dynamic long-range stress field around them, just as the atomic level stresses do [23, 24]. Thus LCE's can interact through the dynamic elastic field they create [30]. For instance they could shield each other to cancel the long-range elastic field to reduce the elastic energy. The increase in the τ_M / τ_{LC} ratio below T_A may be related to such interactions among LCE's. The definition of

LCE as the elementary excitation in the high-temperature liquid state opens the possibility of describing the dynamics of low-temperature liquids in terms of interactions among LCE's. The way the ratio, τ_M / τ_{LC}, increases below T_A is related to fragility [7]. Therefore fragility as well as the approach to the glass transition could be explained in terms of the interactions among LCE's. Incidentally, when the liquid flow is induced by applied stress below T_g, bond creation and annihilation are locally coupled to form a bond-exchange action, so that the τ_M / τ_{LC} ratio is equal to 1/2 [20].

In conclusion we studied the dynamics of simple metallic liquids through classical as well as *ab-initio* MD simulations. We discovered that the dynamics of the local excitations in the atomic connectivity network determines the macroscopic viscosity of a liquid at high temperatures. The local configurational excitations (LCE's) in the atomic connectivity network are the elementary excitations in liquids, and their competition against phonons determines the cross-over phenomenon in liquids. The atomistic picture of liquid flow thus attained illustrates the importance of atomic dynamics in liquid flow, and will impact the way we perceive and describe the flow of liquid.

We thank S. Sastry, S. Yip, J. S. Langer, J. Bellissard, K. Kelton and J. R. Morris for useful discussions. The work was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Materials Science and Engineering Division. *Ab intio* calculations used resources of the National Energy Research Scientific Computing Center, which is supported by the Office of Science of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

References:

1. M. Born, K. Huang, *Dynamical theory of crystal lattices* (Clarendon Press, Oxford, 1954).
2. R. Zwanzig, *Phys. Rev.* **156**, 190 (1967).
3. D. C. Wallace, *Phys. Rev. E* **57**, 1717 (1998).
4. A. Sommerfeld, *Mechanics of Deformable Bodies* (Academic Press, New York, 1964).
5. W. G□tze, *Complex Dynamics of Glass-Forming Liquids* (Oxford University Press, Oxford, 2009).
6. P. Debenedetti, F. H. Stillinger, *Nature* **410**, 259 (2001).
7. C. A. Angell, *Science* **267**, 1924 (1995).
8. D. Kivelson, S. A. Kivelson, X. Zhao, Z. Nussinov, G. Torjus, *Physica A* **219**, 27 (1995).
9. D. Srolovitz, K. Maeda, V. Vitek, T. Egami, *Phil. Mag. A* **44**, 847 (1981).
10. W. Kob, H. C. Andersen, *Phys. Rev. E* **51**, 4626 (1995).
11. Y. Q. Cheng, E. Ma, *Progr. Mater. Sci.* **56**, 379 (2011).
12. Y. Q. Cheng, E. Ma, H. W. Sheng, *Phys. Rev. Lett.* **102**, 245501 (2009).
13. P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
14. http://www.vasp.at/
15. S. Nosé, *J. Chem. Phys.* **81**, 511 (1984).
16. W. G. Hoover, *Phys. Rev. A* **31**, 1695 (1985).
17. *e.g.*, J.-P. Hansen, I. R. McDonald, *Theory of Simple Liquids* (Academic Press, New York, 2006).
18. A. Furukawa, K. Kim, S. *Saito, H. T*a**na**ka, *Phys. Rev. Lett.* **102**, 016001 (2009).
19. R. Yamamoto, A. *Onuki, Phys. Rev*. ***E*** **58**, 3515 (1998).
20. T. Iwashita, T. Egami, *Phys. Rev. Lett.*, **108**, 196001 (2012).

21. R. D. Mountain, R. Zwanzig, *J. Chem. Phys.* **44**, 2777 (1966).

22. T. Egami, K. Maeda, V. Vitek, *Phil. Mag. A* **41**, 883 (1980).

23. T. Egami, *Progr. Mater. Sci.* **56**, 637 (2011).

24. T. Egami, D. Srolovitz, *J. Phys. F* **12**, 2141 (1982).

25. A. F. Ioffe, A. R. Regel, *Prog. Semicond.* **4**, 237 (1960).

26. S. Hosokawa, M. Inui, Y. Kajihara, K. Matsuda, T. Ichitsubo, W.-C. Pilgrim, H. Sinn, L. E. Gonzalez, D. J. Gonzalez, S. Tsutsui and A. Q. R. Baron, *Phys. Rev. Lett.* **102,** 105502 (2009).

27. S. Sastry, P. Debenedetti, F. H. Stillinger, *Nature* **393**, 554 (1998).

28. P. Bordat, F. Affouard, M. Descamps, F. Müller-Plathe, *J. Phys.: Cond. Mat.* **15**, 5397 (2003).

29. V. A. Levashov, T. Egami, R. S. Aga, J. R. Morris, *Phys. Rev. E* **78**, 041202 (2008).

30. K. Trachenko and V. V. Brazhkin, *J. Phys.: Cond. Mat.* **21,** 425104 (2009).

Table 1 Values of τ_∞ and activation energy at temperatures above T_A, E_a, of τ_M for three models. The KA model has a different energy scale.

Model	τ_∞ (fs)	E_a (meV)
Fe	15.3	270
Cu-Zr	19.3	192
Zr-Cu-Al	23.0	181

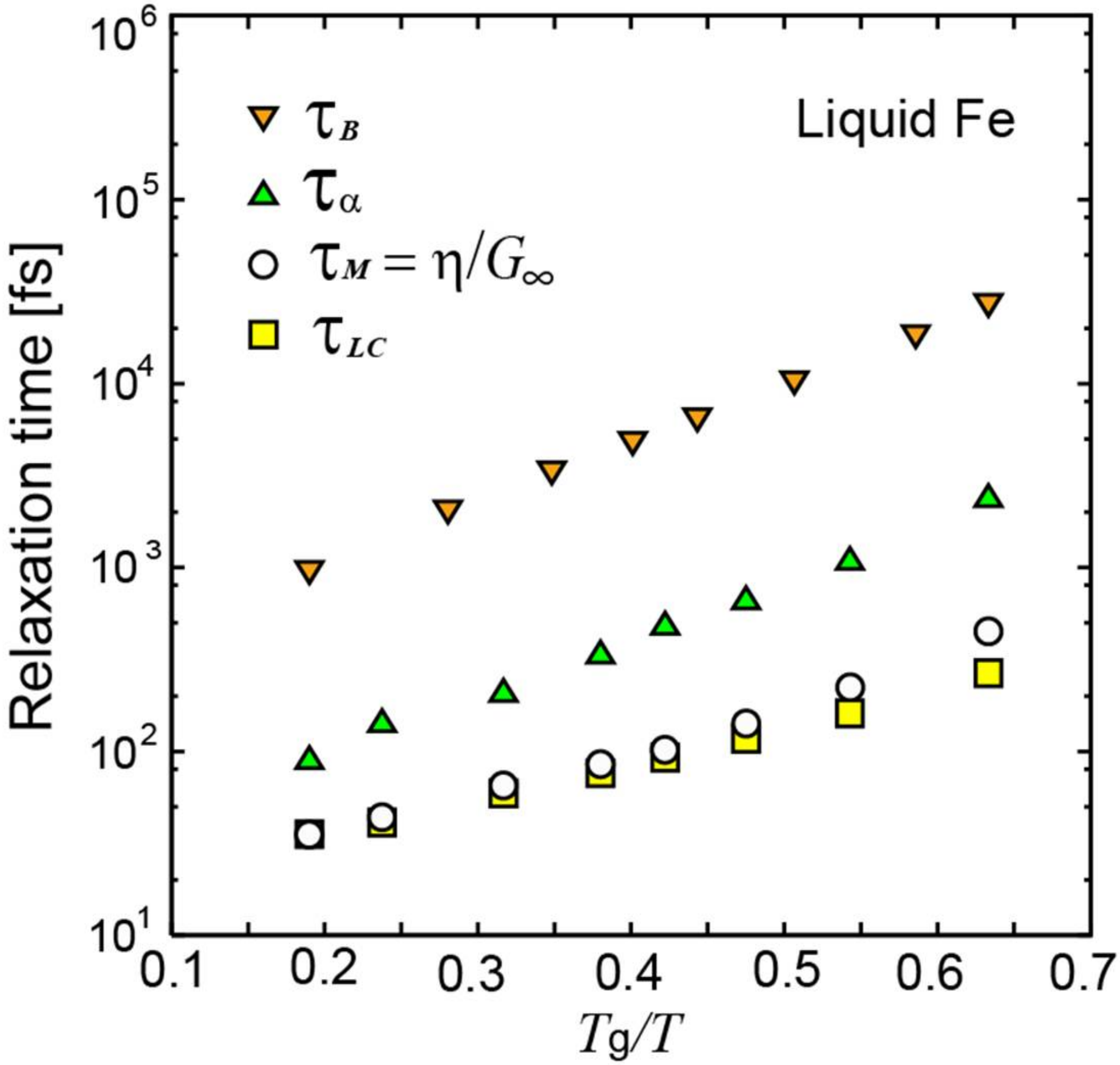
Figure captions:

Figure 1. Bond lifetime, τ_B, α-relaxation time, τ_α, Maxwell relaxation time, τ_M, and the lifetime of local atomic connectivity, τ_{LC}, calculated for liquid iron as a function of T_g/T, where T_g = 950K and T is temperature. See text for the definition of each relaxation time.

Figure 2. Change in the local atomic connectivity by losing or gaining one nearest neighbor.

Figure 3. Temperature dependence of the Maxwell relaxation time, τ_M, and the lifetime of local atomic connectivity, τ_{LC}, calculated for various models of liquid as a function of $1/T$. T_A is the crossover temperature above which the Arrhenius behavior is observed.

Figure 4. The ratio, τ_M/τ_{LC}, plotted against T/T_A for various models, including the results of the *ab-initio* MD simulation for Cu-Zr. Above T_A, τ_M is approximately equal to τ_{LC} for all systems. T_l is the temperature at which $\xi_p = c_T \tau_M$ becomes equal to a, the nearest neighbor distance. Agreement between T_l and T_A suggests that the crossover phenomenon is determined by the ability of crosstalk between the neighboring atoms by the phonon exchange.



Liquid Fe
τ_B
τ_α
$\tau_M = \eta/G_\infty$
τ_{LC}
Relaxation time [fs]
10^1
10^2
10^3
10^4
10^5
10^6
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Tg/T

Fig. 1

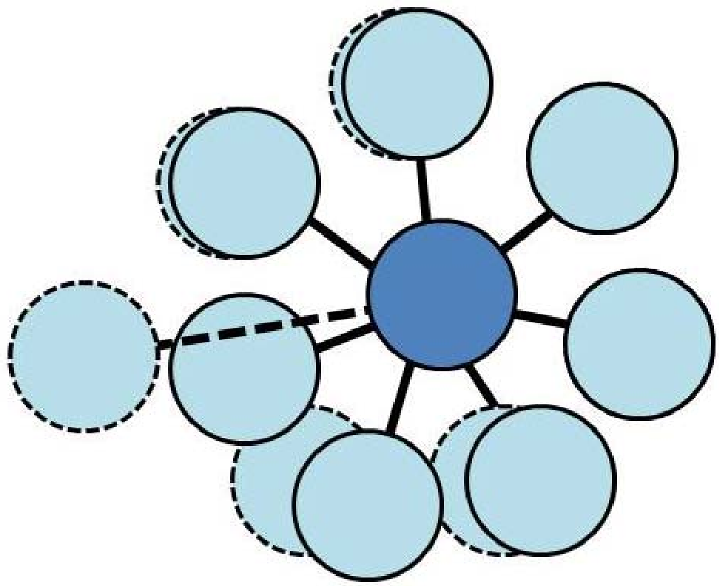
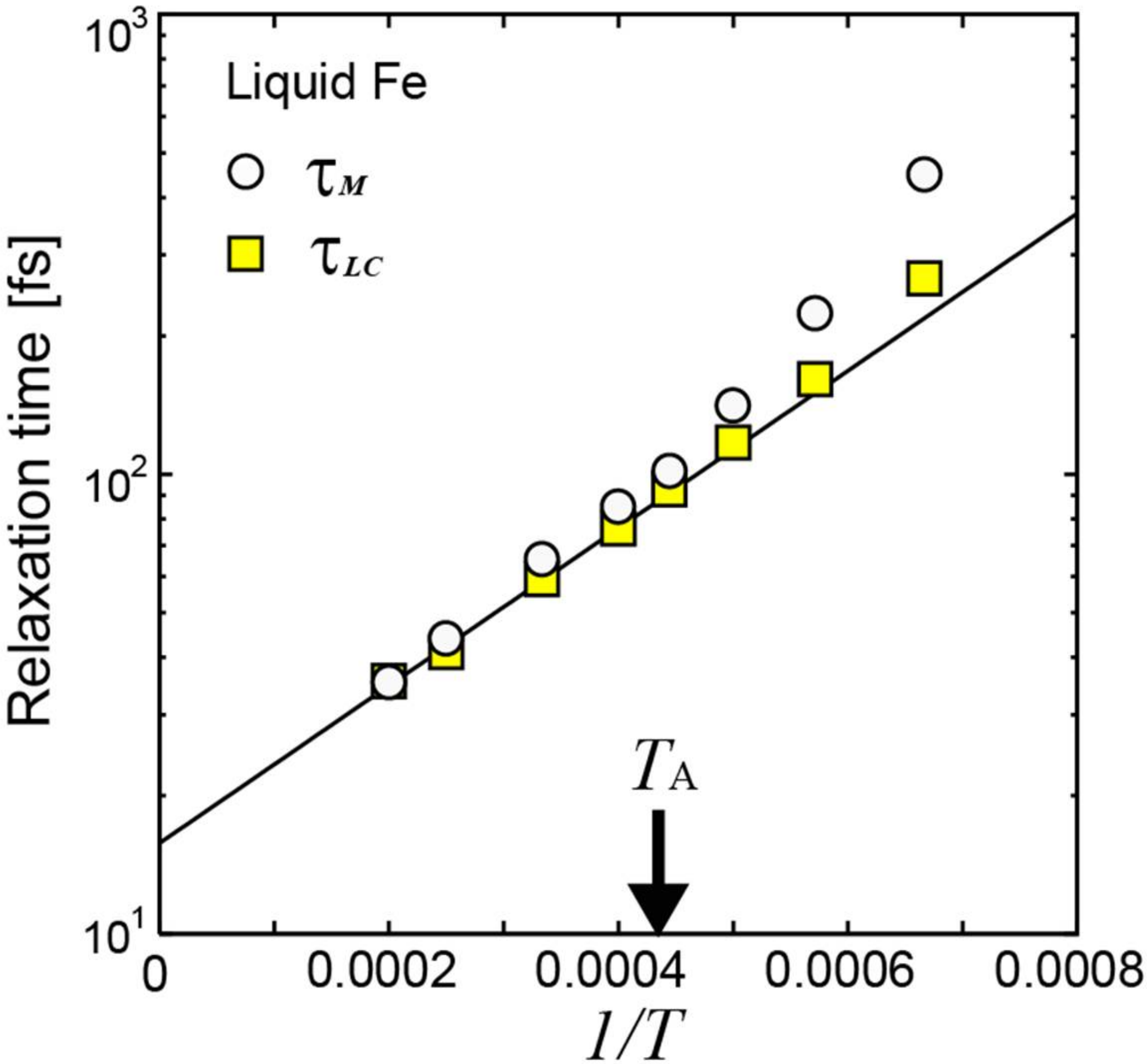
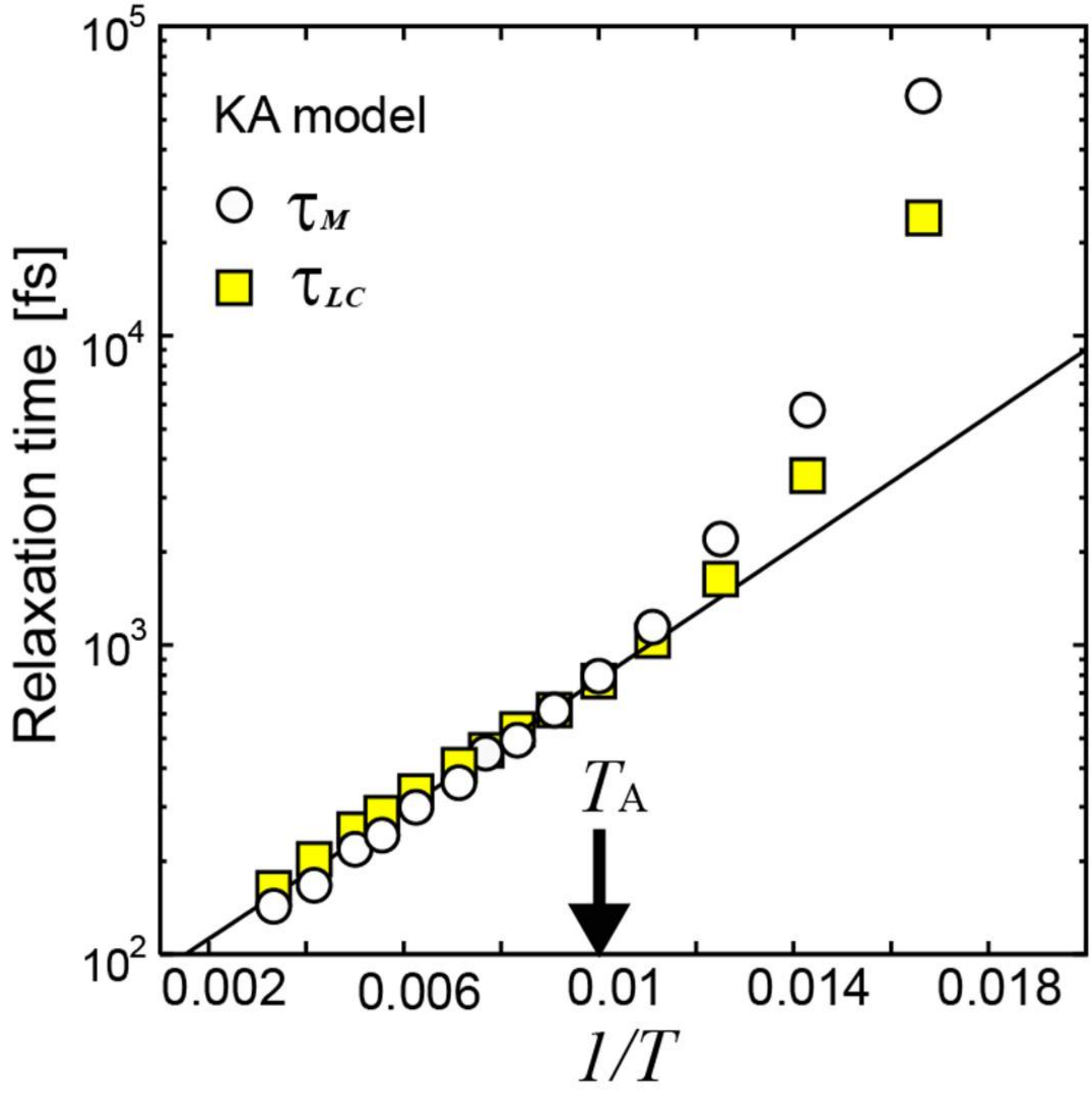


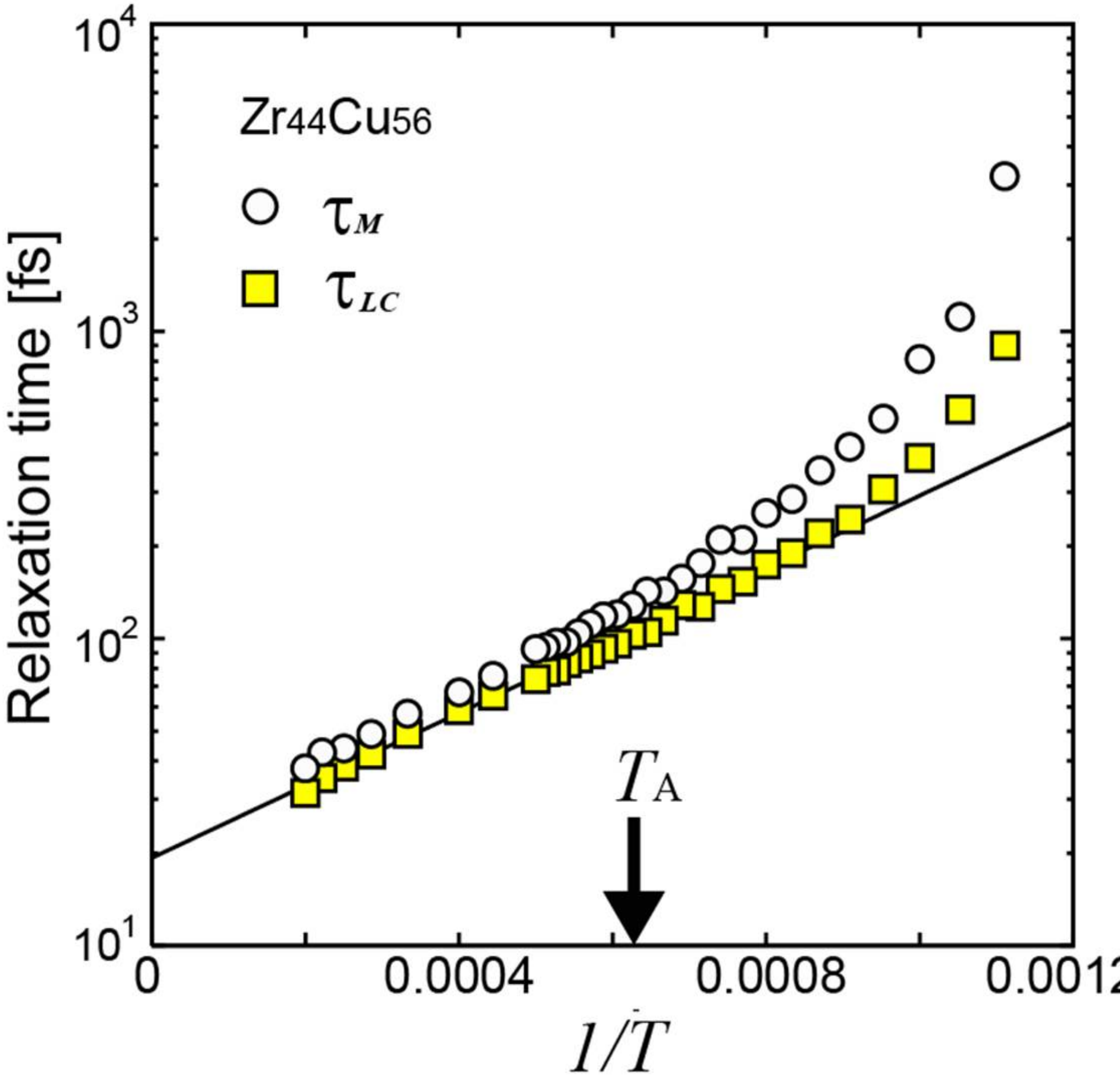
Fig. 2



Liquid Fe
τ_M
τ_LC
Relaxation time [fs]
10^3
10^2
10^1
T_A
0
0.0002
0.0004
0.0006
0.0008
1/T



KA model
τ_M
τ_{LC}
Relaxation time [fs]
10^5
10^4
10^3
10^2
T_A
0.002
0.006
0.01
0.014
0.018
$1/T$


Zr44Cu56
τM
τLC
Relaxation time [fs]
10^4
10^3
10^2
10^1
TA
0
0.0004
0.0008
0.0012
1/T

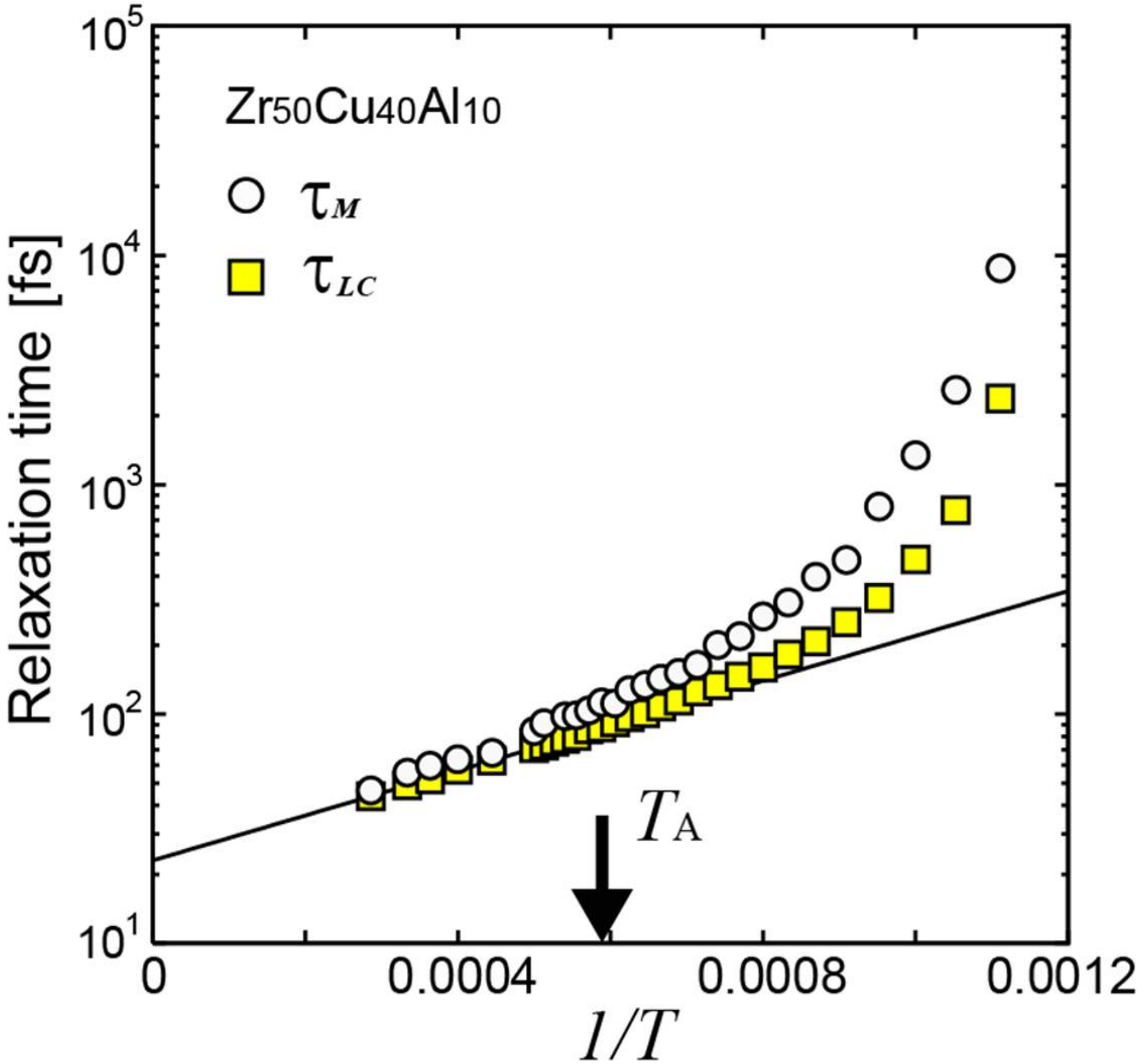
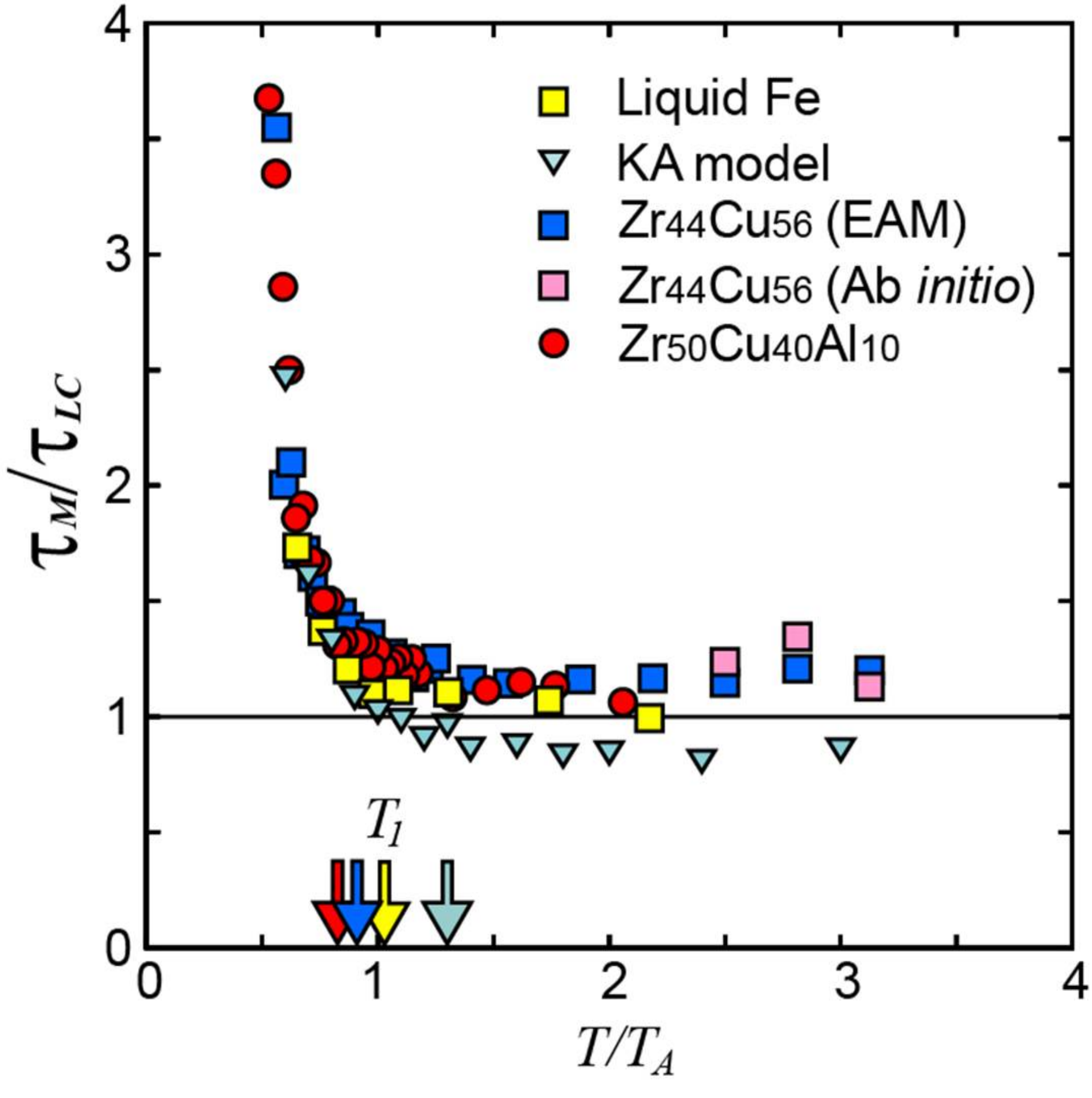

Zr50Cu40Al10
τM
τLC
Relaxation time [fs]
10^5
10^4
10^3
10^2
10^1
TA
0
0.0004
0.0008
0.0012
1/T

Fig. 3



Liquid Fe
KA model
Zr44Cu56 (EAM)
Zr44Cu56 (Ab initio)
Zr50Cu40Al10
τ_M/τ_{LC}
T_l
T/T_A

Fig. 4