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On limitations of the viscosity versus temperature plot for glass-forming substances

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ABSTRACT

The plot scaling of viscosity by the reduced temperature as an important and vivid representation of the liquid fragility property has been utilized by materials scientists for more than four decades. In the present manuscript we discuss practical limitations on the high temperature part of the viscosity plot. It is valid up to the boiling point at pressure ranges from the triple point to the critical pressure and nearly up to the critical temperature at high pressure. Although, the high temperature viscosity estimation at $T \to \infty$ is rather a result of overestimation of an Arrhenius or VFTH equitation fitting and does not have a physical meaning more attention is required to shed light on the behavior of glass-forming liquids in this temperature range by taking into account the supercritical liquid phenomenon.

It is easy to supercool a liquid below its liquidus temperature (T_l) owing to kinetic reasons related to difficulties in the crystal nucleation and growth at low temperature. This is the way glasses are made. At the same time, significant superheating of a solid above its melting temperature and a liquid above its boiling temperature is less likely because the diffusion processes in solids close to the melting temperature, and especially in liquids, are very fast providing no such kinetic limitations to the phase transformation, except for the thermodynamic energy barrier for nucleation of the high-temperature liquid or gaseous phase, respectively. Thus, it is possible to preserve a disordered atomic state of liquid on cooling forming a glass but it is impossible to retain a liquid in the condensed state above its boiling temperature, at least the metallic one, for a sufficiently long time at ambient pressure. Also, an entropy catastrophe was predicted when the entropy of a superheated crystal exceeds that of the liquid phase as an ultimate stability limit for superheated crystals [1].

The plot scaling viscosity by the reduced temperature at ambient pressure introduced by Laughlin-Uhlmann [2] and extended by Angell [3] is a very good illustration of the temperature (T) dependence of an equilibrium liquids' viscosity (η) normalized by its glass-transition temperature (T_g) in a wide temperature range (Fig. 1a) though the extrapolation towards the high-temperature range [4] was not initially considered for the logarithm viscosity vs. T_g/T plot [2]. This plot is a very useful picture illustrating the difference between so-called "strong" and "fragile" liquids especially important for glass formers [4,5]. Here one can see that various liquids exhibit different degrees of deviation from the Arrhenius law:

$$\eta = \eta_0 \exp(Q/RT) \quad (1)$$

(where Q is the activation energy for viscous flow in J/mol and R is the gas constant) in the supercooled liquid state down to T_g which is generally called "fragility". It is also defined using the parameter $m = d(\log(\eta))/d(T_g/T)$ at T_g [6]. The equilibrium viscosity of the glass-forming liquids tends to 10^{12} Pa s at T_g but is not equal for different materials [7]. For a numeric representation of ηF (T) dependence below T_l a famous Vogel-Fulcher-Tammann-Hesse (VFTH) equation [8–10]:

$$\eta = \eta_0 exp[D \times T_0/(T - T_0)] \quad (2)$$

where η_0, D (as an indicator of the fragility) and T_0 are the fitting parameters, and other equations are used [11,12]. At the same time above T_l the equilibrium viscosity of liquid pure metals, for example, obeys the Arrhenius law in a wide temperature range (though a limited range where the measurements were made) [13,14] and tends to the values of 10^{-3}–10^{-4} Pa s if extrapolated to $T_l/T = 0$ (Fig. 1b).

The origin of fragile behavior should be connected with structural changes in the supercooled liquid leading to the variation in the activation energy for viscous flow. For example, intensification

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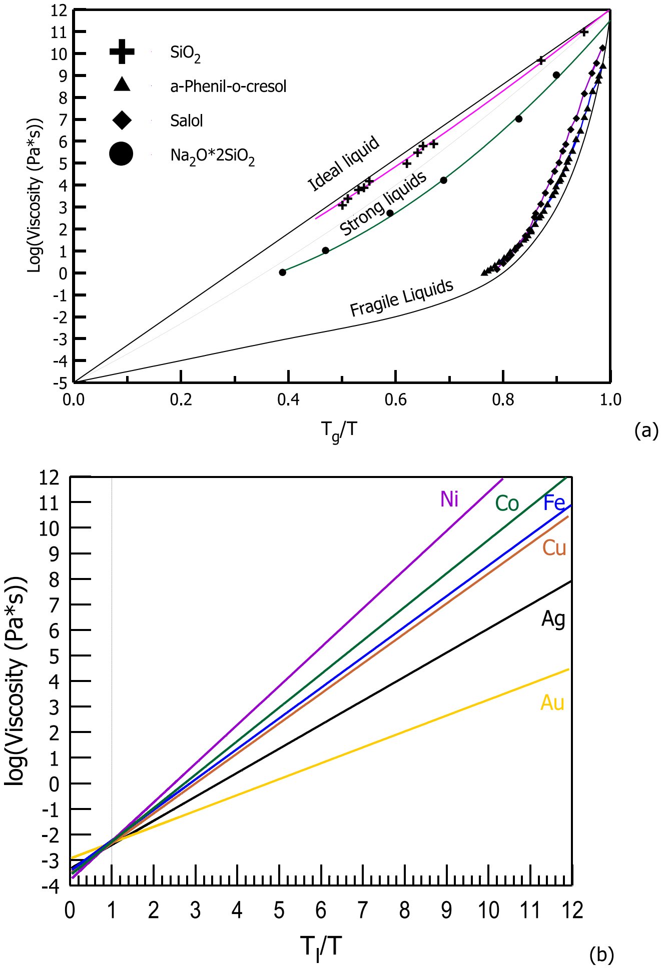

Fig. 1. (a) The viscosity as a function of temperature plot. Black solid lines outline the viscosity values ranging from 10^{-5} to 10^{12} Pa·s typical for strong and fragile liquids [4, and references within Ref. 4 for the data]. The "ideal liquid" shows the Arrhenius behavior. (b) Extrapolation of the equilibrium viscosity of pure liquid metals [13,14] owing to the Arrhenius equation.

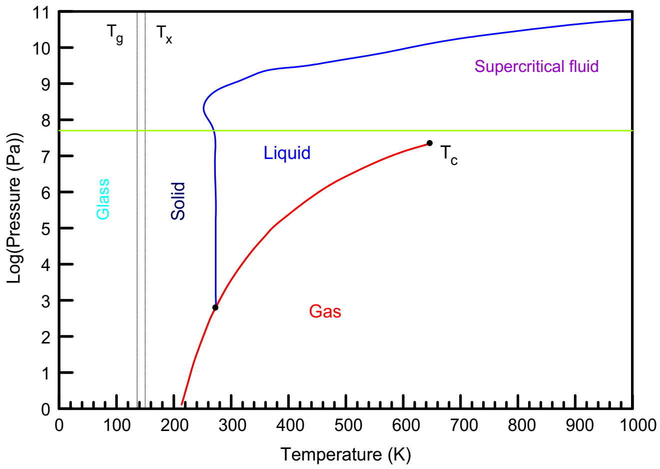

Fig. 2. Schematic representation of the phase diagram of water [24,25]. T_g and T_x represent the glass-transition and crystallization temperatures, respectively. The horizontal green line corresponds to the constant pressure of 50 MPa.

of the covalent bonding between metallic atoms and P was found in Pd-Cu-Ni-P melts in-situ cooled down to the glass-transition region [15] which was responsible for the changes in the structure of a liquid (clustering [16]), and thus, "fragile" behavior of this melt. The influence of liquid fragility on the glass-forming ability (GFA) directly follows from the viscosity plot in Fig. 1a. Even at the same values of the reduced glass-transition temperature ($T_{rg}=T_g/T_l$) more fragile liquid is going to have a lower viscosity in the entire range between T_l and T_g. This lower viscosity of the melt promotes both nucleation and growth processes of crystals [17]. Although fragile liquids are generally predisposed to have lower GFA compared to strong liquids [18] Pd-based alloys still have good GFA owing to their exceptionally high T_{rg} values.

The plot in Fig. 1a constructed for different liquids has two converging points, one of about 10^{12} Pa·s at T_g another one approaching 10^{-4}–10^{-5} Pa s at infinitely high temperature [4]. Although, as it was suggested [19] pure metals likely form most fragile metallic liquids, such transition metals as Ni, Co and Fe should faster attain high viscosity values on cooling than the others (Fig. 1b), owing to their high activation energy for viscous flow. It is particularly why these metals also showed the best glass-forming ability among pure metals on vitrification from the liquid [20]. Although, one should note that Ni was also reported to have a low resistance to subsequent crystallization. On the other hand, not all of the substances reach the equilibrium viscosity of 10^{12} Pa s at the glass-transition temperature monitored by the heat capacity variation, and, in general, this value ranges from about 10^{10}–10^{12} Pa s [21,22]. It is also suggested that glass transition itself may be a kind of critical phenomenon [23].

Looking at high-temperature (low inverse temperature) region of the plot in Fig. 1a one can say that for a liquid, in order to be able to attain a high temperature and retain its liquid state boiling must be avoided. This is possible provided that the liquid is under an overcritical external pressure. Here one should note that pressure effects are very important in liquids. According to a phase diagram for a pure substance (a substance of constant composition that is homogeneous and has constant properties throughout the sample), as it is shown in Fig. 2 for pure water [24,25], liquid phase can exist only above the triple point in pressure axis, otherwise only the thermodynamically stable solid and gaseous phases can exist for a sufficiently long period of time (except for some substances with high binding energy like ionic liquids, for example). Thus, the viscosity plot is generally applicable for a substance above its triple point in a wide pressure ranges for metals [26].

However, there is another important point as a function of pressure (P_c) and temperature (T_c) called the critical point below which the high-temperature part of the viscosity plot also cannot exist. The critical point is the point above which one cannot distinguish between the liquid and gaseous phase though possibility of a liquid-like to gas-like behavior transition above the Frenkel line in the supercritical pressure region is discussed for liquids [27] and particularly for liquid Fe [28]. Only above this point the liquid/gaseous phase can reach high temperatures without undergoing boiling phase transformation before it transforms to a plasma as another high-temperature limitation. One should note that according to Table 1 [29] P_c values are well above the ambient pressure for metals and boiling is expected on heating. However, these pressures and temperatures are practically accessible for alkaline and alkaline-earth metals and it should be possible to perform such heating experiments.

Even if a substance is exposed to an overcritical pressure another problem arises. The structure of a supercritical substance is found to be non uniform. For example, neutron diffraction has shown that tetrahedral liquid-like states are observed in supercritical water above a threshold density, while below this threshold density gas-like water forms small, trigonal, sheet-like configurations [30]. The temperature dependence of viscosity of a supercritical water obtained from Ref. [31] is shown in Fig. 3a. These results indicate that the viscosity of equilibrium water shows a temperature dependence which is well fitted with the