**Interpretation of the apparent activation energy of glass transition**

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**Abstract**

The temperature dependence of the viscosity of glass is a major concern in glass research. The apparent activation energies obtained from Arrhenius plots often show unusual values larger than bond energies, which makes the interpretation of the activation energy difficult. In this study, a reasonable interpretation of the apparent activation energy is obtained along similar lines as those adopted in solid state physics and chemistry. In contrast to the widely held view that the transition occurs at the reference temperature $T_0$ according to the Vogel–Fulcher–Tammann formula, in this work the structural change observed at the calorimetric temperature $T_g$ is considered as a transition from the liquid to solid phases. The energy barrier for atom rearrangements significantly changes in the transition range with width $\Delta T_g$. This change in the energy barrier alters the manner in which the apparent activation energy constitutes the Arrhenius form. Analysis of available experimental data shows that the real value of energy barrier is significantly smaller than the apparent activation energy, and the obtained values are in the reasonable range of energy expected for chemical bonds. The overestimation of the apparent activation energy depends on the ratio $T_g/\Delta T_g$, which is larger for fragile glasses than for strong glasses. Importantly, the linear term in the temperature dependence of the energy barrier does not appear in Arrhenius plots. This explains why the temperature dependence of viscosity for strong glasses obeys well the Arrhenius law, despite that the temperature dependence of energy barrier is expected for every glass.

1. Introduction

The core problem in glass research at present is what is the nature of the glass transition [1–4]. Grass transition is observed, for example, from specific heat ($C_p$) versus temperature ($T$) curves. The transition temperature $T_g$—some authors call it calorimetric transition temperature—is the temperature at which the specific heat exhibits a quick change. It can be experimentally observed, but its value varies to some extent depending on experimental conditions such as the cooling rate. This dependence leads researchers to consider that $T_g$ is not an intrinsic property of glass. It is thought that, unlike the usual phase transitions, structural relaxation plays a crucial role in glass transition: the status of experimental studies on the relaxation is given in review papers [5–8].

The structural relaxation is reflected in the behavior of viscosity $\eta$. The viscosity of glass-forming liquids increases drastically by more than ten orders of magnitude when the liquid temperature approaches $T_g$ from higher temperatures (figure 1(a)). The $T$ dependence of viscosity is most commonly expressed by the Vogel–Fulcher–Tammann (VFT) formula [9–11],

$$\eta(T) = C \exp\left(\frac{D}{T - T_0}\right),$$

where $C$, $D$, and $T_0$ are material-dependent constants. $T_0$ is obtained by extrapolation, many researchers have attempted to identify its significance as the genuine transition temperature, which is an intrinsic property of a glass. Yet another
characteristic temperature is identified as the so-called Kauzmann temperature $T_K$, which is defined as the intersection of entropy $S$ between the supercooled liquid and crystal (figure 1(c)): this intersection is, however, obtained by extrapolating $S$ of the supercooled liquid below $T_0$. The relation of $T_0$ with $T_K$ is being actively debated [13–19].

For normal liquids, the $T$ dependence of viscosity is well understood as a thermally activated process, which obeys the Arrhenius law,

$$\eta(T) = \eta_0 \exp \left( \frac{Q_a}{k_B T} \right),$$

where $k_B$ is Boltzmann’s constant, and $\eta_0$ is a material-dependent constant. In this equation, $Q_a$ has a meaning of the activation energy. This formula has been derived from quantum mechanics [21]. For normal liquids, values $Q_a$ are of the order of a few tenths of electron volts or less [22], which is a reasonable range, on account of the chemical energies of materials. If this standard formula equation (2)) is applied to the viscosity of glasses in a narrow range of temperature, values $Q_a$ are found to be surprisingly large, more than 1 eV (in some cases 10 eV), even for organic glasses whose melting temperature $T_m$ is less than room temperature [23–25]. There is no convincing theory to interpret the large values of $Q_a$. Furthermore, the pre-exponential factor $A = 1/\eta_0$ is extremely large: typically, the magnitude is of the order of $10^{20}$ [25]. Thus far, no theory that accounts for the extraordinarily large values have been established.

Figure 1. Glass transition represented in terms of (a) viscosity $\eta$ and (b) specific heat $C_p$. (c) Shows entropy $S$ versus $T$ curves for liquid (l), supercooled liquid (sl), glass (g), and crystal (c). Dashed curves indicate extrapolations from the supercooled-liquid state.
Presently, researchers attempt to find a physical meaning in the activation energy in the form of normalizing $T$ with $T_g$ in the Arrhenius plot, which is widely known as the Angell plot [26, 27] among many other methods [28–30]. In the normalized form of the Angell plot, how largely the $T$ dependence of $\eta$ deviates from the Arrhenius law is the main information that can be obtained; fragility is a parameter used to quantify the degree of the deviation. Depending on the fragility, glasses are classified as strong or fragile. This manner of analysis is useful for classifying glasses. However, it does not aid the chemical interpretation of the activation energy, which is the basic element for understanding properties of materials. Although there are attempts to find relationships between the activation energy to fragility or other quantities [31–35], the problem of large values $Q_a$ has not been solved. Without a pertinent interpretation of the activation energy, one could not understand why the viscosity of glass changes so largely when approaching $T_g$. This study is aimed at establishing appropriate interpretation of $Q_a$ obtained from the Arrhenius plot.

A resolution of the problem of the activation energy of glass came from a very different context, namely, the state variables of glass. Today, it is a standard view that glass states are nonequilibrium states. However, although the glass transition is in fact a nonequilibrium phenomenon—transition itself represents nonequilibrium—unduly emphasizing the nonequilibrium character hinders the thermodynamic nature of glass. A frequently-claimed reason for the nonequilibrium character is that the state of glass is not determined by temperature and pressure ($P$) only but is affected by the previous history of treatments. Thermodynamics states are to be specified solely by the current values of state variables. If the glass states were equilibrium, the properties must be uniquely determined solely by $T$ and $P$, provided that these two are only the state variables, but this is not the case, from which the above conclusion is deduced. However, the attribution of this discrepancy to nonequilibrium state is an easy escape from the difficulty. Careful observation reveals that the dependence of the past treatment that the solid underwent is a common property of solids: e.g., the mechanical properties of metals are affected by the past heat treatments; even Si wafers have dependence on the past history. Any solid has, to a certain degree, the dependence of its properties on the preparation conditions [36]. The fundamental question then is which quantities, other than $T$ and $P$, can be the state variables of a solid: here the term thermal equilibrium coordinate (TC) is used for state variable. This question was at times considered by several authors to be a flaw of the theory [37–39], but has not been solved until recently. The author reappraised this problem by starting from the definition of equilibrium and TCs for solids. In short, the answer to the question of TCs for a solid is the time-averaged positions $\bar{R}$, of all the constituent atoms of the solid: the time-averaged positions $\bar{R}$, but not instantaneous positions $R(t)$ are stressed [36, 40]. This conclusion is also valid for the state during glass transition, provided some restrictions are imposed. The thermal response of solids is so fast—typically 10 ps—that slow changes in the structure are adiabatically decoupled with fast vibrational motions. This behavior is expressed as the adiabatic approximation of the second kind [40]. Then, the instantaneous state at timescales much longer than the response time of vibrations can be regarded as an equilibrium state, i.e. temporal equilibrium [40]. The states during glass transition are states of temporal equilibrium. During such a transition, all the averaged positions $\bar{R}(t)$ as well as the time-dependent temperature $T(t)$ are well defined, and accordingly the glass state is expressed by the instantaneous values of all TCs.

A striking consequence of this conclusion is that the energy barrier $E_b$ of the structural change of a glass during glass transition is determined solely by the present positions of atoms, $E_b = E_b(\{R\})$, irrespective of the previous history. Owing to the relaxation of atoms, the current positions $\{R\}$ cannot be uniquely determined by the current value $T$: the effect of this relaxation is the cause of the hysteresis. To the first-order approximation, however, it is allowed to regard $E_b$ as a function of $T$, i.e. $E_b(T)$. This $T$ dependence invalidates the conventional Arrhenius analysis, which assumes $Q_a$ to be constant. Hence, the apparent activation energies obtained from the Arrhenius plot does not indicate the real value of $E_b$ [41].

In this paper, the above conclusion regarding the temperature dependence of $E_b(T)$ is justified by analyzing experimental data on viscosity. On the basis of this analysis, a pertinent interpretation of the apparent activation energy is provided. In a previous study [41], this interpretation was derived from an analysis of the hysteresis in the $C-T$ curve. Viscosity measurement is a more direct method to obtain the activation energy. The rest of this paper is organized as follows: the theoretical basis for the present analyses is given in section 2. Then, section 3 shows the first evidence for the proposed interpretation based on the relationship between the width of glass transition and the apparent activation energy. The second evidence is obtained by directly evaluating the temperature-dependent energy barrier: this evidence is described in section 4, which provides three examples of different classes of glasses. An important implication of the present results to glass transition is discussed in section 5. Section 6 concludes the study. Throughout this paper, the numerical values of viscosity $\eta$ are presented in terms $\log \eta$ (poise) with base of 10.

2 This accords with the spirit of the local equilibrium ansatz for solids. For the present case, the spatial variation of $T$ is not needed to consider.
2. Theoretical backgrounds

2.1. Glass state and glass transition

There exists a large gap in comprehension of the glass state between glass physics and other areas of solid state physics. For non-experts for glass research, glass is evidently a solid. The glass transition that occurs at \( T_g \) is a phase transition between the solid and liquid phases. However, glass researchers do not think so. Many of glass researchers consider glass as a special type of liquid, specifically, \textit{kinetically frozen liquid} [42]. Hence, it is necessary at the outset to declare the present view [40, 41] and to show the differences from the views of glass literature.

The signature of the glass transition is observed in a profound change in the properties of glass, such as specific heat and thermal expansion, in a narrow range of temperature [43]. Here, the range is specified by \( T_{g,1} \) and \( T_{g,2} \) with its width \( \Delta T_g = T_{g,2} - T_{g,1} \), as shown in figure 1(b), and is called transition region [44]. In this paper, the term \textit{glass state} is restricted to refer to the phase of a glass substance below \( T_{g,1} \), and is regarded as a solid phase. Above \( T_{g,2} \), and below \( T_m \), the state of the glass substance is a supercooled-liquid state; there \( C_p \) obeys almost the classical limit of Dulong-Petitte law, \( 3R \) (\( R \) is the gas constant) [45]. The state between \( T_{g,1} \) and \( T_{g,2} \) is referred to as \textit{the transition state} [44]. The \( C_p-T \) curve often exhibits complicated shapes depending on the preparation conditions, which makes it difficult to identify the width \( \Delta T_g \). Usually, an averaging value is used for \( T_g \) unless special interest is paid for the width. In spite of the preparation dependence, it is meaningful to discuss the unique value for \( T_g \) within a reasonable range, provided suitable conditions are used [46, 47]. In contrast, the temperature dependence of viscosity \( \eta \) has no characteristic temperature other than \( T_0 \) when \( \eta(T) \) is recasted to the VFT form: however, it will be shown in section 4.1 that this is not necessarily true. Operationally, the \( T_g \) can be defined as the temperature at which \( \log \eta = 13 \). Many of glass researchers do not think that there is a sharp boundary between the supercooled-liquid state and the glass state. Even in the glass state, atoms are migrating with extremely slow velocities. From this, \( T_g \) is not considered as the temperature of a transition. Instead, \( T_0 \) in equation (1) deserves the genuine transition temperature, below which the so-called \textit{ideal glass} appears. The reason that the ideal glass has not been observed is attributed to its extremely slow motions. Consequently, it is considered that the observed glass is thermodynamically a nonequilibrium state.

The difference of the above contrasting views is rooted in understanding of the fundamentals of thermodynamics: the definition of equilibrium and TC. The rigorous definition of equilibrium has been only recently established [48], which enables us to define TC in a consistent manner. The author applied this principle to solids, concluding that the equilibrium positions of all the atoms \( \{ \mathbf{R}_j \} \) are TCs for solids [36]. The present views for glass are based on this general conclusion [40]. The important points relevant to this study are listed below, with contrasting the general views in glass research [2–4, 49–51]: however, for some points, consensus is not necessarily obtained also in glass researchers.

1. \textit{Glass is a solid}: it is viewed as a frozen liquid in the glass literature. An often-claimed reason for the lack of distinction between the liquid and glass states is that atomic positions are random in both states. However, this is only true when the instantaneous positions of atoms \( \mathbf{R}_j(t) \) are compared. Thermodynamically, equilibrium positions \( \mathbf{R}_j \), which are obtained by time averaging, have sense. They are well defined for solids and glasses too, but undetermined for liquids.

2. \textit{Glass is an equilibrium state}: it is viewed as a nonequilibrium state in the glass literature. This is the natural consequence of the preceding conclusion. Although the changing state in the course of time during the transition is in fact a nonequilibrium state, the values of TCs can be specified for each moment. When the change in the external conditions is halted and keep it constant for a time longer than the relaxation time, the transition state finally reaches the equilibrium state even at \( T \) in the transition region.

3. \textit{The transition state is a mixture of liquid and solid phases}: it is viewed as a supercooled-liquid state after a sufficiently long time in the glass literature. Although the two views are different regarding the equilibrium states, they share the common thought that the transition region is a \textit{crossover} region between different phases. The term \textit{dynamic heterogeneity} in the glass literature is also compatible with the present view of the mixed state.

A natural consequence of the above-described views is that the energy barrier \( E_b \) for atomic movement depends on the structure, that is, \( E_b = E_b(\{ \mathbf{R}_j \}) \), meaning that \( E_b \) varies strongly in the transition region from \( E_{b,g} \) in the solid state to \( E_{b,l} \) in the liquid state [41]. The atom relaxation (the time delay of atom rearrangements) breaks a one-to-one correspondence between \( \{ \mathbf{R}_j \} \) and \( T \), which brings about hysteresis. When the rate of change in \( T \) is slow enough, however, the effect of hysteresis is suppressed at minimum, and \( E_b \) can be regarded as a function of \( T \). The following analyses use the relation \( E_b = E_b(T) \). Nonetheless, it should be stressed that the relation \( E_b = E_b(T) \) is only an approximation. The idea of the \( T \)-dependent energy barrier was at times proposed
in early studies [20, 52–55]. The $T$-dependent $E_b$ in the present study is definitely different from them in the physical grounds. Recent studies by molecular-dynamic simulations show evidence for the $T$-dependent energy barrier [56, 57]. Unfortunately, these simulations did not give the value of $E_b$, and hence the problem why glasses have large $E_b$ has been left unsolved.

2.2. Theory of viscosity

Many theories have been proposed for explaining the viscosity of glass since Eyring derived the quantum-mechanical formula for viscosity of liquids [21, 58]. These theories have been reviewed in textbooks by Nemilov [28] and Rao [59]. The current trend of study has shifted to microscopic dynamics, which is modeled by, for example, the mode-coupling theory, dynamic facilitation, and first-order random transition [1–4, 49, 51, 60, 61]. The present study, however, remains at a macroscopic level based on the reaction rate theory, focusing on how real values of the energy barriers are obtained from the Arrhenius plot.

For normal liquids, formula equation (3), including the pre-exponential factor $\eta_0$, can be deduced from the microscopic theory, without assuming any model [21, 58]. Rate theory by Eyring explains well the viscosity of normal liquids [22]. For an isotropic media, the pre-exponential factor $\eta_0$ in equation (2) is expressed as

$$\eta_0 = \left( \frac{a_0}{\lambda} \right)^2 \frac{h}{a_0^3} \frac{Z_0}{Z_{av}},$$

(3)

where $a_0$ is the mean interatomic distance and $\lambda$ is the average distance between the equilibrium positions of the original and slipped states. The product $(\lambda/a_0)^2a_0^3$ may be interpreted as the activation volume $V_{av}$, which is the volume swept by the slipped atoms. Planck’s constant $h$ is a universal constant but can be replaced by a material constant $k_B T/
u_0$ at thermodynamic equilibrium, where $\nu_0$ is the mean frequency of the phonon spectrum at $T$ and is interpreted as the attempt frequency. $Z_0$ and $Z_{av}$ are the partition functions of the normal and the activated states of the slipped states, respectively. Although it is difficult to calculate the partition function $Z$, the values of $Z$ enter in equation (3) through the ratio $Z_{av}/Z_0$, which is of the order of unity in most cases, and hence, we can ignore this term. By assuming $\lambda \approx a_0$, $\eta_0 = h/V_0$ gives $\log \eta_0 = -3.5$ for $V_0 = 10 \, \text{Å}^3$. This result is well in agreement with the experimental results: in many cases, $\log \eta_0 = -3$ to $-4$ [62]. The activation energy $Q_a$ is of the order of 0.1 eV or less [22, 62].

For solids, the definition of viscosity is not so simple because of its nonlinearity. Nevertheless, the rate theory of Eyring was widely applied to solid dynamics beyond the original object of viscosity. Plastic deformation of crystalline solids is explained by the rate theory, in which the slip motion is mediated by dislocations [63]. For the case of metallic glass, the slip motion is mediated by free volumes [64] or by shear transformation zones [65]. Although the physics involved in the processes is different from those of liquids, the formal expression for the rate of deformation is the same as equation (3), if the quantities in this equation are suitably interpreted. Hence, there is no reason not to apply this formula for glasses. However, the problem in this case is that the material-dependent ‘constants’ are not constant during the transition, because a transition is a process of structural change.

Naturally, the energy barrier $E_b$ must change in the transition region. The change in $E_b$ is expected for strong glasses too. Experimental facts are different: $\eta(T)$ seems to obey well the Arrhenius law, implying no change in energy barriers. Thus, it is important to solve this contradiction. The apparent activation energy $Q_a^*$ is obtained from the derivative of $\ln \eta$ with respect to $1/T$,

$$Q_a^* = \frac{\partial \ln \eta}{\partial (1/T)}.$$  

(4)

Here, an asterisk is attached to $Q_a$ in order to stress the apparent value. We are so accustomed to this formula to obtain energy barriers in numerous applications that we seldom consider how the Arrhenius form is altered when the energy barrier has $T$ dependence. Let us consider a simple case of the linear dependence of the energy barrier

$$E_b(T) = E_{b,0} - b(T - T_g),$$

(5)

otherwise constant. Here, $b = (E_{b,0} - E_{b,1})/\Delta T_g$ is a constant. In the Arrhenius form, the linear term in $T$ is canceled by the denominator in the exponent of equation (2). Thus, equation (3) becomes

$$\eta(T) = \eta_0 e^{-b/T_e} \exp \left( \frac{Q_a^*}{k_B T} \right),$$

(6)

where $Q_a^* = E_{b,0} + b T_{g,1}$. Hence, the $T$ dependent term is dropped from the Arrhenius form. Instead, a large separation between $Q_a^*$ and $E_b$ appears. Since $\Delta T_g$ is small, $Q_a^*$ is approximated by
The factor \( k = T_g / \Delta T_g \) plays a role of a magnification factor for the barrier height. Although the linear term disappears from equation (7), its Arnold term \( e^{b/k_B T} \) contributes to the transport coefficients through the \( T \)-independent term \( e^{b/k_B} \) in a manner similar to equation (6). However, the above derivation shows that it is not appropriate to interpret the \( e^{b/k_B} \) term by entropy. In fact, \( b/k_B \) often becomes as large as 100. It is impossible to explain this magnitude by entropy alone. Even for vaporization, the increase in entropy is at most of the order of 10. To obtain the real energy barrier \( E_b \), the term \( e^{b/k_B} \) should be retained in the Arrhenius analysis. One way to obtain the real value of \( E_b \) is use of

\[
Q_a^e \approx \frac{T_g}{\Delta T_g} (E_b - E_{b0}).
\]

provided that \( \eta_0 \) is independent of \( T \). Unfortunately, \( \eta_0 \) is not expected to remain constant during the glass transition. The size \( \lambda \) of the moving unit is strongly correlated with the coherent length \( \xi \), and the latter changes significantly near the transition temperature \([66]\). In addition, the ratio \( Z_n/Z_a \) may not be ignored because the moving units become more collective motions for solids. This problem has to be solved.

3. Width of glass transition

The present theory predicts that the apparent activation energy \( Q_{a}^e \) is magnified by the factor \( k = T_g / \Delta T_g \). Let us examine this magnification in \( Q_{a}^e \) by analyzing the experimental data. The data for this aim are taken from measurements of the specific heat. While numerous data have been accumulated for \( T_g \), data for \( \Delta T_g \) are very rare. The width is sensitive to the shape of the \( C-T \) curve in the transition region, which is largely affected by the conditions of sample preparation and measurement \([47]\). It is, therefore, important to use the references in which the experimental conditions are well documented. Moynihan compiled data of \( \Delta T_g \) for 17 inorganic glasses with their \( T_g \) well above room temperature \([67]\). These glasses include chalcogenides, heavy-metal fluorides, and network oxide glasses. He took special care when collecting experimental data: i.e. only the data obtained under common conditions, such as within an acceptable range of heating rate, were considered. He found that there is a good correlation between \( Q_{a}^e \) in viscosity measurement and \( \Delta T_g \) in heat-capacity measurement

\[
\frac{Q_{a}^e}{k_B} \Delta \left( \frac{1}{T_g} \right) = 4.8 \pm 0.4.
\]

The values of \( Q_{a}^e \) are obtained in the range \( 11 \leq \log \eta(T_g) \leq 12 \), where the \( T \) dependence of viscosity obeys the Arrhenius law. The relationship between \( T_g/\Delta T_g \) and \( Q_{a}^e/k_B T_g \) which is taken from Moynihan’s data is plotted in figure 2. The acronyms and the chemical compositions are explained in his paper. There is a good correlation between \( T_g/\Delta T_g \) and \( Q_{a}^e/k_B T_g \).
From the approximation of equation (7), equation (9) is rewritten as

$$\frac{E_{b,i} - E_{b,i}}{k_B T_g} = 4.8.$$  \hspace{1cm} (10)

This ratio seems reasonable when compared with the range of energy barrier $E_b$ of impurity diffusion. In silica glass, the energy barriers $E_b$ of impurity diffusions are reported to range from 0.3 to 0.8 eV [68]. Since for silica glass $T_g = 1450$ K, the ratio $E_b / k_B T_g$ ranges from 2 to 6. Although diffusion and viscose motions are different modes of motions, the energy barriers should not be so different [69, 70]. Thus, the relationship shown in equation (10) must give reasonable values for $E_b$. This infers that the previous values for the activation energy for glass transition were significant overestimations.

A definition of fragility, among various methods available, is $m = (\partial \ln \eta / \partial (1/T)) / k_B T_g$, meaning the activation energy normalized with the glass-transition temperature [71]. Hence the relationship equation (9) is also rewritten as follows:

$$m = 4.8k.$$  \hspace{1cm} (11)

Although this factor 4.8 was determined from a certain group of glasses, this may not largely change among various glasses: Ito et al showed that this is indeed the case [14]. Thus, one can immediately see that fragility represents the magnification factor $k$. Therefore, the greater fragility, the more magnified $Q^*_a$ is compared to the true value $E_b$. Therefore, fragile glasses exhibit large $Q^*_a$ in spite of their low melting temperatures. This naturally leads to the following interpretation of fragility: that is, it represents how rapidly the energy barrier varies with varying $T$. This interpretation is more appealing because the energy barrier is the standard terminology in solid state physics and chemistry. A similar interpretation for the $m$ was inferred by Dyre and Olsen [31]. The present study gives an alternative meaning of $m$ as the magnification factor for the activation energy. Researchers attempted to find correlations between fragility with other properties of glasses. Fujimori and Oguni found the correlation of $m$ with a special index representing the difference between $\alpha$ and $\beta$ relaxations [72]. Scopigno et al. found another correlation of $m$ with the decorrelation of the density fluctuations [73]. These correlations can be understood better by using a familiar term, energy barrier.

4. Analysis of the temperature dependence of viscosity

4.1. Silicate glass

Let us examine the full-scale temperature dependence of viscosity for three classes of glasses. The first class of glasses comprises silicate glasses, which are typically strong glasses. It is said that the $T$ dependence of $\eta$ for strong glasses obeys the Arrhenius law, but it is true only in a relative sense compared with fragile glasses. If the $T$ dependence of $\eta$ is examined over a wide range of $T$, one sees a large variation in the activation energy: for example, the $Q^*_a$ of silica glass increases from 4.0 eV above $T = 2000\, ^\circ\text{C}$ to 8.1 eV at $T = 1400\, ^\circ\text{C}$ as temperature declines [29, 74–76].

Figure 3 shows the apparent activation energies $Q^*_a$ obtained using the conventional method of equation (4) for soda-lime-silicate (SLS) glass, as reported by several authors. The chemical composition of SLS glass is formally $\text{SiO}_2 : \text{Na}_2\text{O} : \text{CaO} = 75 : 15: 10$, and the transition temperature $T_g$ is $530\, ^\circ\text{C}$. The numerical data of $\ln \eta(T)$ were retrieved from the original figures by using a digitizer. The retrieved data were then processed by fitting them with smoothing functions, and $Q^*_a$ was obtained by taking the derivatives of the fitting function according to equation (4). As seen in figure 3, the apparent activation energy $Q^*_a$ increases as temperature decreases to $T_g$. As the temperature approaches $T_g$, $Q^*_a$ reaches about 6.8 eV and then quickly decreases. The maximum value is more than twice the value at $T = 1200\, ^\circ\text{C}$. The linearity in the Arrhenius plot holds only for the range of $11 \leq \ln \eta \leq 14$, which corresponds to a temperature range of $600\, ^\circ\text{C} \geq T \geq 500\, ^\circ\text{C}$. This behavior of $Q^*_a$ on cooling, namely, first increasing in the liquid region, then reaching the maximum at the transition, and finally decreasing in the solid region, is observed also in the self-diffusion of oxygen in SLS glass [77].

Let us calculate the corrected value $E_b$ according to equation (8). The constant $\eta_0$ is not known. The lowest value of the measured viscosity cited above is about $\ln \eta = 2$, which was reported by Lullie [78]. The pre-exponential factor $\eta_0$ is less than this value but is larger than a typical value of normal liquids, i.e. $-3.5$. Since silicate glasses are among the most viscous materials, tentatively, $\ln \eta_0 = 0$ was used. The calculated values are plotted in figure 4. The maximum value of $E_b$ reduces significantly to 2.2 eV from the corresponding value $Q^*_a$ of 6.8 eV. This $E_b$ value of 2.2 eV is already smaller than the Si–O bond energy of SiO$_2$ (4.6 eV). If an increase in $\eta_0$ with decreasing $T$ is taken into account, the value $E_b$ is further reduced. The $E_b$ value can also be estimated by using equation (7). For the transition width $\Delta T_g$ of the SLS glass, the value of NBS710 ($T_g / \Delta T_g = 17$, as shown in figure 2) is adopted. Equation (7) leads to $E_{b,d} \approx E_{b,j} = 0.37\, \text{eV}$. The model shown in equation (5) assumes that the change in $E_b$ occurs only within $\Delta T_g$. However, as seen in figure 4, the change in $E_b$ begins from far higher temperatures and is more gradual against $T$. In this respect, equation (7) may be an overcorrection. The true
value $E_b$ lies between 0.37 and 2.2. For the self-diffusion of oxygen in silica glass, the energy barrier is 2.3 eV [83], and hence the value about 2 eV for $\eta$ is reasonable.

A notable observation in figure 4 is the temperature dependence of $E_b$ below $T_g$. It is not easy to measure viscosity values larger than $\log \eta_0 = \log 13$. Despite this difficulty, viscosity below $T_g$ were measured even in early studies [79, 84, 85]. For SLS glass, Jones reported a significant reduction in $Q_a^*$ from 2.3 eV above $T_g$ to 0.25 eV at $T = 350^\circ$C, at which $\eta$ increases to about $\log \eta = 18$ [79, 85]. The values reported by Jones are shown in figure 3; the plotted values are obtained by a smoothing functions, and hence the values are slightly different from the values reported by Jones. A similar reduction was reported by Shen et al [86]; a reduction from $Q_a^* = 5.2$ eV above $T_g$ to 1.2 eV at $T = 450^\circ$C was observed for SLS glass. Surprisingly, on applying the correct form of equation (8), these quick reductions in $Q_a^*$ below $T_g$ are drastically alleviated so that they are nearly constant, as shown in figure 4. This is consistent with the present model shown in figure 1(c). This behavior is reasonable because the structure does not change once the glass substance is frozen. There are some literatures describing the activation energy as being saturated around $T_g$ [28, 87], which means a recovery of the Arrhenius law below $T_g$. Recently, Kawamura et al performed viscosity measurements at temperatures as low as 270 $^\circ$C, which may be the lowest temperature ever reported for silicate glasses [82]. They employed the fiber-bending method, which was developed by Koide [88]. They performed measurements for a simulated high-level radioactive waste (HLW) glass. The main difference between HLW and SLS glasses is inclusion of $B_2O_3$ in HLW. Hence, it is reasonable to observe that the viscosity of HLW glass was lower than that of SLS glass. If, for Kawamura’s data, log $\eta_0$ is calculated to make $\eta(T)$ constant below $T_g$, the pre-exponential factor is obtained as log $\eta_0 = 10.4$, as indicated by the green line in figure 4.

Figure 3. Apparent activation energy $Q_a^*$ of silicate glasses obtained by the conventional method. Data are for soda-lime-silicate (SLS) glass samples, except for Kawamura’s data. Kawamura’s sample is a high-level radioactive waste (HLW) glass. The sources of data are as follows: Lillie [78], Jones [79], Napolitano [80], Mazurin [81], and Kawamura [82].

Figure 4. Energy barrier $E_b$ of SLS glass. The same symbols as those used in figure 3 are used here. All data are calculated by assuming $\log \eta_0 = 0$. Under the assumption that $\log \eta_0 = 10.4$, the corrected values for Kawamura’s data are reduced to the green line.
and hence the apparent activation energy $Q_a^*$ have low-melting temperatures that are near or lower than room temperature. Most of them are fragile glasses.

The next class of glasses to be examined comprises organic glasses. Generally, the glasses belonging to this class can, however, be corrected by the present theory. By applying equation (4), $Q_a^*$ becomes as small as 0.1 eV, when $\lambda$ is ignored. Now, it is clear that the large values of the apparent activation energy $Q_a^*$ that are common for organic glasses can be ascribed to the narrow width $\Delta T_g$, see figure 5. In this case, $\lambda$ is close to even that of silicate glass. In the literature, this large value of $Q_a^*$ is obtained by different ways depending on the definition of the activation energy: apparent activation energies exceeding 10 eV are found [25]. In this study, \( \rho \)-terphenyl is examined as an example of organic glasses. This is because the viscosity of this material was measured in a wide range from log $\eta = -0.5$ to 13, which covers the whole range of the Angell plot. Glass transition occurs at $T_g = 239$ K with the width $\Delta T_g = 5$ K. For model calculations of the $T$ dependence of \( \rho \)-terphenyl, see [28]. The inset of figure 5 shows $Q_a^*$ of \( \rho \)-terphenyl as obtained by the conventional method using equation (4). The data $\eta(T)$ were retrieved from Nemilov’s textbook (figure 44 of [28]): the plot data actually consist of three sets of data provided by Laughlin, [29] Greet, [92] and Cukierman [93]. The apparent activation energy $Q_a^*$ increases up to $4$ eV, which is close to even that of silicate glass. In the literature, this large $Q_a^*$ for organic glasses is at times explained by the collective modes of a large slipping units. This explanation is not convincing. A collective mode can alter $\Delta T_g$ in the pre-exponential factor in equation (3). However, each atom constituting the slipping unit receives equally thermal energy $k_B T$, and hence the activation energy per atom is almost the same. This unreasonably large value can, however, be corrected by the present theory. By applying equation (8), a significant reduction from $Q_a^*$ is obtained. This is shown in figure 5. In this case, log $\eta_0 = -2$ is used. The maximum $E_b$ is 0.8 eV, which is within a reasonable range of the energy barrier. If the multiplication factor, in this case $k = 50$, is adopted, the value $E_b$ becomes as small as 0.1 eV, when $E_{bl,j}$ is ignored. Now, it is clear that the large values of the apparent activation energy $Q_a^*$ that are common for organic glasses can be ascribed to the narrow width $\Delta T_g$.

4.2. Organic glass

The next class of glasses to be examined comprises organic glasses. Generally, the glasses belonging to this class have low-melting temperatures that are near or lower than room temperature. Most of them are fragile glasses, and hence the apparent activation energy $Q_a^*$ strongly depends on $T$. When $T$ approaches $T_g$, from high temperatures, $Q_a^*$ increases quickly, as shown in the Angell plot. Large values of $Q_a^*$ are reported at $T_g$ e.g., $Q_a^* = 5.5$ eV for glucose [23] and 2.5 eV for salol [91]. More examples are provided in the review by Hodge, who has presented many values of $Q_a^*$ evaluated by different ways depending on the definition of the activation energy; apparent activation energies exceeding 10 eV are found [25]. In this study, \( \rho \)-terphenyl is examined as an example of organic glasses. This is because the viscosity of this material was measured in a wide range from log $\eta = -0.5$ to 13, which covers the whole range of the Angell plot. Glass transition occurs at $T_g = 239$ K with the width $\Delta T_g = 5$ K. For model calculations of the $T$ dependence of \( \rho \)-terphenyl, see [28]. The inset of figure 5 shows $Q_a^*$ of \( \rho \)-terphenyl as obtained by the conventional method using equation (4). The data $\eta(T)$ were retrieved from Nemilov’s textbook (figure 44 of [28]): the plot data actually consist of three sets of data provided by Laughlin, [29] Greet, [92] and Cukierman [93]. The apparent activation energy $Q_a^*$ increases up to $4$ eV, which is close to even that of silicate glass. In the literature, this large $Q_a^*$ for organic glasses is at times explained by the collective modes of a large slipping units. This explanation is not convincing. A collective mode can alter $\Delta T_g$ in the pre-exponential factor in equation (3). However, each atom constituting the slipping unit receives equally thermal energy $k_B T$, and hence the activation energy per atom is almost the same. This unreasonably large value can, however, be corrected by the present theory. By applying equation (8), a significant reduction from $Q_a^*$ is obtained. This is shown in figure 5. In this case, log $\eta_0 = -2$ is used. The maximum $E_b$ is 0.8 eV, which is within a reasonable range of the energy barrier. If the multiplication factor, in this case $k = 50$, is adopted, the value $E_b$ becomes as small as 0.1 eV, when $E_{bl,j}$ is ignored. Now, it is clear that the large values of the apparent activation energy $Q_a^*$ that are common for organic glasses can be ascribed to the narrow width $\Delta T_g$.

4.3. Metallic glass

The third example comprises metallic glasses. Metallic glasses have fragility intermediate between that of strong covalent glasses and fragile organic glasses [94]. The apparent activation energy $Q_a^*$ of the glass transition of metallic glasses ranges from 2 to 8 eV near $T_g$ [95]. The plastic deformation of crystalline materials is mediated by dislocations, whereas for metallic glasses it is mediated by the so-called shear transformation zone (STZ) [65]. The approach for describing the $T$ dependence of the viscosity is opposite to that employed in section 2.2, where the starting state is the liquid state. For the area of metallic glasses, the study starts from the solid state [96]. The formula for viscosity is formally the same as that given in equation (2). The activation volume $V_a^*$ is considered to be that of an STZ. For ZrTiCuNi glass, a typical STZ includes 20–30 atoms. [96].

All the presented data were measured by independent authors and by different methods. Therefore, the agreement between the values of $E_b$, below as well as above $T_g$, validates the reliability of the obtained $T$ dependence. The energy barrier $E_b$ becomes saturated below $T_g$. By taking all the above results together, it is likely that $E_b$ of SLS glass is no more than 2 eV. Furthermore, the present analysis shows that no divergence occurs at $T_g$. This conclusion agrees with the conclusions of recent studies on the glass transition [19, 89, 90].
The temperature dependence of the viscosity has been gleaned from recent experiments on metallic glasses. A theoretical model was proposed by Johnson et al, who considered a formula for the energy barrier based on the elastic moduli of the solid state and extended it to the liquid state [95, 97] (a similar study was reported [98]). They adapted the exponential decay for the $T$ dependence of the energy barrier, obtaining a formula

$$\frac{\eta}{\eta_0} = \exp\left(\frac{W_e}{k_B T} \exp\left[2n(1 - \frac{T}{T_g})\right]\right),$$

(12)

for $T > T_g$. Here, $W_e$ is the energy barrier at $T = T_g$ and $n$ is a fitting parameter whose value is the order of unity [95]. When $T$ approaches $T_g$, the term exp $[2n(1 - T/T_g)]$ in equation (12) can be expanded with respect to $\Delta T = T - T_g$, resulting in

$$\frac{\eta}{\eta_0} = \exp\left(\frac{W_e}{k_B T} \left(1 + 2n - 2n \frac{T}{T_g}\right)\right).$$

(13)

This has the same form as the linear approximation of equation (5) with a magnification factor $k = 1 + 2n$. Numeric examples are given by them: for Pd$_{77.5}$Cu$_{16.5}$Si$_{6.5}$, $T_g = 634$ K, $\log \eta_0 = -2.11$, and $n = 1.67$. This leads to the magnification factor $k$ of 4.3. Hence, the correction for $E_b$ is not too large compared with those of other classes of glasses.

An interesting point regarding metallic glasses is that viscosity below $T_g$ is sometimes measured because of the practical interest in the creep phenomenon. Taub and Spaepen found that the activation energy $Q_{a}^{g}$ of viscosity of Pd$_{82}$Si$_{18}$ is almost constant at about 2.0 eV in a temperature range from 420 to 540 K [99]; Pd$_{82}$Si$_{18}$ is a metallic glass with $T_g = 634$ K [100]. Interestingly, the value $Q_{a}^{g}$ does not change by annealing at various temperatures. This is consistent with the present assumption, equation (5). There is no sign to exhibit the divergent behavior of the VFT law in this case too.

5. Discussion

Although transition is not the focus of this study and is a too big issue to discuss in an article, the findings of this study have important implications to this issue. On account of the quite novel ideas of the present study, it is desirable to leave some comments on the glass transition. The analyses in section 4 showed that none of the experimental data on viscosity below $T_g$ showed sign of exponential divergence at a finite temperature. Careful analyses on the temperature dependence on viscosity show that the asymptotic form of $\eta(T)$ already begins to deviate from the VFT form at the vicinity of $T_g$ [101]. Recent experimental studies reported non-divergence in this range [19, 89, 90].

Both $T_0$ and $T_k$ are obtained by extrapolating viscosity and entropy, respectively, measured at $T > T_g$. This extrapolation loses its validity when one accepts the experimental transition occurring at $T_g$ as a genuine phase transition. Nobody considers that, for an ideal gas, an extrapolation of the temperature dependence on viscosity below $T_g$ is almost constant at about $2.0 \text{ eV}$ in a temperature range from 420 to 540 K [99]; Pd$_{82}$Si$_{18}$ is a metallic glass with $T_g = 634$ K [100]. Interestingly, the value $Q_{a}^{g}$ does not change by annealing at various temperatures. This is consistent with the present assumption, equation (5). There is no sign to exhibit the divergent behavior of the VFT law in this case too.

6. Conclusion

In usual phase transitions of crystal/liquid, the energy barrier for atomic movement changes abruptly: the transition occurs at a fixed temperature $T_{mo}$, which hides the change of energy barrier from observation. In contrast, for glass transition, continuous structural change occurs in a certain range of temperature with the width $\Delta T_g$. This structural change causes a change in the energy barrier $E_b$ in a continuous manner, and this causes $\eta(T)$ to deviate from the Arrhenius law. In particular, the effect of cancellation of the linear term in the $T$
dependence of the energy barrier should be taken into account. This causes a large magnification of the observed value of the activation energy $Q_{a*}$.

This prediction has been validated by examining available experimental data. The degree of deviation depends mainly on the magnification factor $k = T_g/\Delta T_g$. Generally, fragile glasses exhibit sharp transitions with narrow widths $\Delta T_g$. This explains the extraordinarily large values for the observed $Q_{a*}$ of fragile glasses; e.g. the magnification factor is of the order of magnitude 50. This magnification also occurs in strong glasses, whereas the magnification factor is not large. In either case, the real energy barrier $E_g$ is estimated to be around 1 eV, which lies in a reasonable range of the chemical energy of liquids and solids. Thus, the present result enables us to interpret the behavior of the viscosity of glass on the same ground of energetic approach that is commonly used in solid state physics and chemistry. The linear $T$ dependence of $E_g$ is of course an approximation. To know the accurate $T$ dependence, the concrete formula for the pre-exponential factor $\gamma_0$ is needed. This is left as future study.

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Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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