

Microscopic-Phenomenological Model of Glass Transition

I. Foundations of the model

(Revised and enhanced version)

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Abstract: The glass transition is described as a time- and history-independent singular event, which takes place in an interval dependent on the distribution width of the molecular vibration amplitudes. Free volume is redefined and its generation is the result of the fluctuating transfer of thermal energy into the condensed matter and the resulting combined interactions between the vibration elements. This creates openings between the elements which are larger than the cross-section of an adjacent element or parts thereof. Possible shifts of molecules or molecular parts through such gaps depend on the size and axis orientation and do not require further energetic activation. After a displacement additional volume is created by delays in occupying abandoned positions and restoring the energetic equilibrium. The different possibilities of axis orientation in space result in different diffusive behavior of simple molecules and chain molecules, silicate network formers and associating liquids. Glass transformation takes place at a critical volume V_{g_0} when the cross-section of the apertures becomes smaller than the cross-section of the smallest molecular parts. The glass transition temperature T_{g_0} is assigned to V_{g_0} and is therefore independent of molecular relaxation processes. T_{g_0} is well above the Kauzmann and Vogel temperatures, usually just a few degrees below the conventionally measured glass temperature $T_{g(qT)}$. The specific volume at the two temperatures mentioned above cannot be achieved by a glass with an unordered structure but only with aligned molecular axes, i. e. in the crystalline state.

Simple liquids consisting of non-spherical molecules additionally alter their behavior above V_{g_0} at V_{g_l} where the biggest gaps are as small as the largest molecular diameter. T_{g_l} is located in the region of the crystalline melting point T_m . Both regions, above and below T_m , belong to different physical states and have to be treated separately. In the region close to V_{g_0} resp. T_{g_0} the distribution of vibration amplitudes has to be taken into account. The evolution of transport properties depend on specific volume and not on temperature per se.

The boundary volume V_{g_0} in conjunction with the distribution width of the molecular vibrations when approaching V_{g_0} is the key to understanding the glass transition.

Key words: Viscosity, glass temperature, glass transition, packing density, glass state, liquid state

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Introduction

Transport properties are one of the key properties for characterizing internal processes in liquids. The molecular-kinetic processes at the transition from liquid to glass have a strong influence on many critical processes in nature and technology, such as volcanism or the physical aging of polymers.

It is not a problem to define the upper limit of the liquid to the gaseous state, but the relations of the liquid state to the vitreous state are not unambiguously clear, of worldwide interest and are considered to be an unresolved problem of solid state physics^{1, 2, 3}.

Since the beginning of the last century, a connection between the liquid and the glassy state has been discussed in such a way that glasses were considered to be "frozen" liquids with long term viscous properties. Especially the glass transition seen as a special feature of the so called dynamic α -process is usually interpreted as a loss of ergodicity between the experimental investigation and the molecular relaxation time on different time scales. According to these ideas, there is no definite glass temperature, but only a glass (transition or transformation) temperature $Tg_{(qT)}$ which depends on the respective cooling /heating rate $qT = (\pm)dT/dt$. For a cooling rate going towards 0, however, a discussion was held, on the idea of a thermodynamically based glass temperature which would correspond to a phase transition of 1st or 2nd order.

Therefore, the challenging question arises as to whether transport properties such as viscosity in the normal liquid range have something to do with the glass state, or in other words: does a function describing the dependence of viscosity on temperature require a limit value parameter above the absolute zero point? The idea that a certain "free volume" between the molecules is the reason for the mobility of liquids already emerged in 1870 with van der Waals' dissertation and experienced a renaissance in the 1950s. However, there is currently no agreement on the type, scope and distribution of this free volume. There is particularly no generally accepted theory on the generation of additional empty space, as even for crystalline solid bodies the occupied space is larger than the corresponding sum of the molecular volumes. Thus it is not surprising that still in the recent years the main work dealing with the glass transition concentrates on temperature dependence and not on dependence on specific volume and thermal expansion.

In 1980, the author developed an equation based on the assumption that relative changes of viscosity (or other transport properties) are proportional to the relative change of the free volume. Due to the (erroneous) simple substitution of V by T , a power equation with 3 material-dependent parameters has been developed, which provides very good results in the calculation of the viscosity values depending on the temperature in polymers and inorganic glasses as well as in super-cooled simple molecular liquids. In addition, one of the parameters was almost perfectly consistent with the Tg values from the literature. In the case of simple molecular liquids in the normal liquid regime, however, large deviations can be observed, which are attributed to the increasing influence of vapour pressure and the resulting internal structural changes. Starting with the development of mode coupling models (MC) published in 1984^{4, 5, 6} leading to a similar power law equation as the author's from 1980, additional to Tg a second dynamic transition above Tg was supposed. As will be shown, the temperature parameter Tc of the MC power law equation has a volume dependent origin and may be better replaced by the value Vg_l presented in this study.

There are a lot of competing theoretical models to the just mentioned (e.g. configurational entropy model of Adam and Gibbs⁷, energy landscape approach^{8, 9}, random first order transition theory¹⁰, entropic barrier hopping, frustration limited domains, shovel model) (s. Cummins et al. 1997¹¹ and Dyre 2006¹²), bond orientational two-order-parameter model (Tanaka 2012¹³), jamming scenarios (Liu and Nagel 1998/2010^{14, 15}). Up to date, however, no consistent theory could prevail without contradiction. Even there are reflections negating any transition but assuming a continuous process

down to absolute zero (Kivelson et al. 1996¹⁶ and recently Hecksher et al. 2008¹⁷, Elmatad et al. 2008¹⁸, Pogna et al.¹⁹). Still today^{1, 20} it is common sight (in the author's view one of the main inadequate treatments leading to erroneous models) to treat the low-viscosity regimes above the melting point of the crystalline phase T_m and the high-viscous states in the supercooled region below T_m as continuum although already in 1958²¹ pre-crystallizing had been discussed to be the cause of changes in the viscosity behavior.

It is well known that self-diffusion as basic transport phenomenon in the normal liquid state is subject to the same temperature and pressure dependence as viscosity and other transport qualities. As self-diffusion is independent from external influences it is generally best suited to show the temperature and pressure dependence. Because of the theoretically stated and experimentally confirmed equivalence between diffusion and viscosity dependence in the liquid range above T_g , and due to the ample data material the following verification deduced from the equations on the new model concept was mainly carried out using viscosity data.

Martinez-Garcia et al.²² recently stressed that the transfer of the results to other transport phenomena should be very likely. The authors agreed with a majority of researchers in recent years that the dielectric coefficient has the same temperature dependence as viscosity. However, due to the different molecular processes - molecular shifts in viscosity and autodiffusion compared to intramolecular deformations in dielectric measurements - there are doubts about the admissibility of a joint treatment. Of course, volumetric relationships play a role in both cases, but the orientation of the molecular axes in space should have a different influence on the measurements. Higher pressures in particular should have different effects on intra- and intermolecular processes. The results of the dielectric measurements, which are said to be more accurate than viscosity measurements, but decouples slightly from the latter when approaching T_g ^{2, 23}, are therefore not included in the study.

It is, according to the author's understanding, imperative and of fundamental importance for the precise prediction of liquid characteristics to include the glass transition into the theory of the liquid state.

Pioneer studies and comprehensive surveys on the subject are presented by Kauzmann 1946²⁴, Fox and Flory 1950/1954^{25, 26}, Rost 1955²⁷, Williams, Landel and Ferry 1955²⁸, Cohen and Turnbull 1961²⁹, Kovacs 1963³⁰, Barlow, Lamb and Matheson 1965³¹, Koppelman 1965³², Plazek et al. 1966/1968/1994/1999^{33, 34, 35, 36}, Davis and Matheson 1966³⁷, Breuer and Rehage 1967³⁸, Kanig 1969³⁹, Goldstein⁸ 1969, Donth 1981⁴⁰, McKenna⁴¹, McKenna and Angell 1991⁴², Böhmer, Ngai and Angell 1993⁴³, Angell 1995⁴⁴, Ediger, Angell and Nagel 1996⁴⁵, Colucci et al. 1997⁴⁶, Rössler et. al. 1998⁴⁷, Ngai 2000⁴⁸, Tarjus and Kivelson 2000⁴⁹, Berthier and Garrahan 2003⁵⁰, Tanaka 2005⁵¹, Dyre 2006¹², Liu and Nagel 2010⁵², Tarjus 2010⁵³, Berthier and Piroli 2011⁵⁴, Chen, Angell and Richert 2012⁵⁵, Stillinger and Debenedetti 2013⁵⁶, Biroli and Garrahan 2013⁵⁷, Langer 2013⁵⁸.

Liquid structure and glass formation

Common Sights of Internal Molecular Mobility in Liquids

The liquid as well as the gaseous state is generally considered a disordered state. According to the widest spread theories regarding the liquid state molecules have to surmount potential barriers by adjoining molecules when flowing. Surmounting is done in activated discrete jumps. Batschinski 1913⁵⁹ seems to be the first to neglect the energetics and develop a simple equation based on the idea of free volume that allows liquids to flow. Ideas regarding the free volume's redistribution free of additional activating energy were also put forward by Hirschfelder et al. 1935⁶⁰, 1954⁶¹, they could, however, not assert themselves. Fox and Flory 1950²⁵, Cohen and Turnbull 1961²⁹ as well as Grest and Cohen 1981⁶² turned again to the idea of a free volume, whereby Cohen and Turnbull underlined, however, with reference to the diffusion theory in Glasstone, Laidler and Eyring 1941⁶³ that part of the molecules of a liquid were in an activated state ("5-10 %"). The molecules would move with gas kinetic velocity and were temporarily captivated in a "cage" formed by adjoining molecules. Due to occasional variations in density, a hole opens up on a cage that is large enough to allow a substantial displacement of the molecule contained in it. A diffusive movement would only then occur when another molecule reached the newly formed empty space before the first molecule returned to its original position. They underlined also that the diffusion in their understanding is not based on activation in the normal sense, but is rather the result of a re-distribution of the free volume within the liquid. In 1967 Chen and Turnbull⁶⁴ reiterate, in accordance with the newly introduced model, that " η depends primarily on configuration rather than temperature per se."

Foundations of the New Microscopic-Phenomenological Model

Origin of internal fluctuations of free volume and implications thereupon

In condensed matter the vibrating elements – molecules, atoms, ions, chain segments – in the matrix are positioned such that the intermolecular attractive and repulsive forces are in equilibrium and free energy is minimized (Mie potential, r_m). That basic principle should be temperature-independent. Input of temperature energy leads to increasing vibration amplitudes. If the distances between the centers of the molecules remain unchanged, the repulsive forces would become greater. In order to maintain the equilibrium of forces, the distances between the centers of the elements must increase - the normal thermal expansion of the solids.

Transfer of thermal energy into the molecular matrix cannot be uniform but fluctuates in time and space. In succession the elements of the matrix vibrate around temporally and locally fluctuating centers and, in immediate consequence, equilibrium of attractive and repulsive forces become disturbed. (see figure 1) As every movement of an element out of its equilibrium position causes a spontaneous evasive movement of the neighbors the whole matrix will be influenced.

As mentioned above, it is the general and undisputed physical view that the molecules in the matrix of condensed matter attempt to reach the most favorable energetically equilibrium position. In the case of spherical molecules, this state, the optimum distance between the molecular centers, should always be present. In the case of non-spherical particles, on the other hand, axis alignment determines the distance between the molecular centers. In a liquid, the molecular axes are not evenly arranged in space and, due to the undirected repulsion forces of the neighboring molecules, tend to rotate in all directions of space. Due to the local mutual hindrances by adjacent molecular fields, however, it should hardly be possible to rotate in a single operation, contrary to conventional opinion. Free rotations would require displacements of neighboring molecules. Assuming that the principle of minimum constraint (Le Chatelier's principle) remains valid even with a kT -excited molecular matrix, this is considered improbable.

The molecules try to position their center of mass on the equilibrium positions, which are characterized by the potential minima, but this is prevented by the irregularly aligned axes. The smallest distances between the molecules are achieved with uniformly arranged axes, i. e. - contrary to the impetus of entropy - in the crystalline state. This energetically preferred state is aimed for at all temperatures by partial revolutions, but temporarily formed structures with aligned axes cannot be consistent at high kT levels. When approaching T_m , more and more clusters withstand the destructive forces of high-energy neighbors and finally crystallites are formed that solidify the entire matrix. Therefore, the rotational possibilities of the vibrating molecules should be crucial for each transition scenario.

From the above situation it follows that when approaching T_m , the number of particles per volume unit decreases, while short-lived clusters of aligned molecules are formed at the same time, thus decreasing the number of translations per time unit and in immediate succession the viscosity. The real behavior of almost all investigated substances seems to confirm this model concept, as the numerical study shows (e. g. for n-pentane, the difference between calculated and observed viscosities at T_m is about 40% compared to the region above T_m+30 K, where the deviations are symmetrically distributed with residuals below 0.1%).

The vibration amplitudes are randomly distributed and penetrations are severely restricted as long as the spatial changes consist only of the vibration space of the normal thermal expansion. A critical event is created by the random occurrence of combined actions of a certain number of elements. Then evasive movements can intensify and create temporary free spaces and openings. The number and size of short-lived openings depend on the temperature and are distributed around an average value. If the gaps are larger than the cross-section of an adjacent element, a shift of this element in principle, wholly or partly with a molecular part, is possible. A further prerequisite that such a change of position can actually occur is the corresponding spatial direction of the adjacent vibration amplitude. Due to their axis-independent orientation, spherical elements should not be subject to any spatial influence, but since the forms of real molecules are only exceptionally ideal spherical, the projection of the molecular form directed to the aperture is decisive, see Fig. 1.

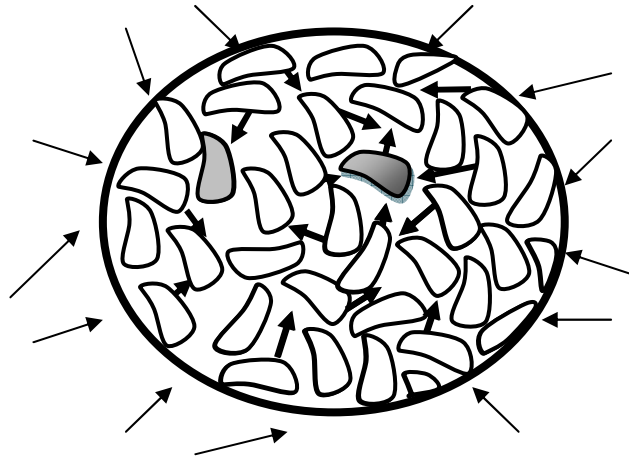


Fig. 1 Diffusion process (schematic – 2D-view).

The long arrows in fig. 1 symbolize the transfer of temperature energy by external impulses of gas molecules or radiation coming from all directions in irregular intervals which stimulates the molecules of the liquid matter to vibrate inharmoniously. The vibration frequencies and amplitudes are distributed around a mean value. The short arrows are to demonstrate that the molecular centers and the axes may tend to move in different directions (the drawn vectors are not correctly arranged). The drawn molecules are to demonstrate the field limitations.

The above picture may appear trivial *prima facie* but it is to emphasize the importance of axis orientation, only rarely taken into consideration³⁷, as crucial for the glass transition physics.

Above a characteristic temperature T_{g_g} , some cavities or gaps are large enough for the (partially) occupation by neighboring molecules, if their vibration directions permit it. In the case of a (partial) occupation, the occupying molecule itself leaves behind an empty position, which can only be occupied again with a time delay until the size and direction of the vibration amplitude of an adjacent molecule is suitable. If the reoccupation at the second position would coincide with the release in the first position, the volume changes would be compensated for each other. However, since the abandoned sites cannot be immediately reoccupied, the system reacts by restoring the equilibrium molecular distances and creates additional volume.

The fact that self-diffusion depends on the proportion of molecular size to kT may be shown by the following (fictive) experiment: (s. fig. 2)

Six white and one black sphere are placed in a circle on a vibrating support. The black sphere is situated in the centre and is encircled by the other spheres. The spheres are surrounded by a circular limitation at a certain distance from the outer virtually enveloping sphere ring. The question comes up, which diameter the limitation must take on so that the black sphere moves out of its central position. In case that distance is less than a certain fraction of the sphere diameter the black sphere will indeed move around its central position, but cannot leave it. If, however, the limitation distance is larger the black sphere will leave its central position the faster the larger the limitation diameter is. In this experiment the limitation symbolizes the average vibratory amplitude of the molecules, and thus kT , and η corresponds to the average shifting velocity. The vibration intensity and frequency concerning the minimum distance of the limitation plays no role during this experiment. They have to be simply big and fast enough. “ T_g ”, the limiting temperature between the solid and the liquid state, is reached when the limitation distance has such a value that the black sphere moves out of the central position. The experiment yields the free volume fraction on a simple way without considering energy foundations.

Fig 2 shows some simple shifting possibilities in dependence of the relation between the radii of the vibrating spheres and the diameter of the outer limitation:

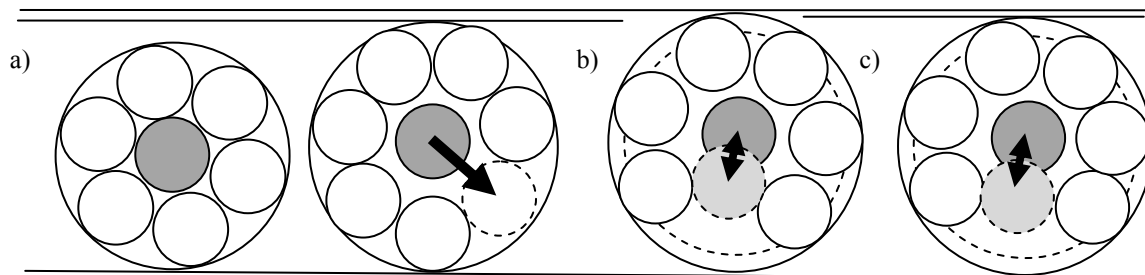


Fig. 2 Geometrical approach to shifting possibilities

In case a) of fig. 2, all spheres first swing radially at the same time and then crowd together along the boundary. This scenario seems extremely unlikely, if not impossible.

Scenario b) seems to be more realistic and raises the question of what minimum distance the limit must be, that at a certain moment a gap opens and the middle sphere moves out of its position. Presumably the situation c) intermediate between a) and b) comes closest to the truth.

The experiment, apart from that, addresses one of the unsolved, probably unsolvable⁶⁵, problems in physics resp. mathematics. It is well known that the tightest packing of spheres will become $1 - 1/6 \pi 2^{0.5} \approx 74\%$ when the spheres are arranged by hand in hexagonal packing. On the other hand when the spheres are poured into a container and are compacted by mechanical vibrations the packing density reaches at maximum about 63%⁶⁶. That means there is no moment where the spheres are packed in the tightest way. If one refers this result to the problem of glass formation one may suppose that the situation depicted in fig. 2c would become very interesting when using non-spherical molecular

adequate bodies with varying elasticity modules instead of hard spheres. This might perhaps explain the influence of the molecular rotation possibilities and the above asked question. Suitable computer simulations should not imply too big a problem.

There is no doubt that viscosity is associated with molecular changes in position, as the equivalence to self-diffusion shows. Furthermore, it should be clear that the number of position changes is strongly temperature-dependent, and since each position change generates a free volume, the viscosity could also be calculated in direct dependence on the temperature. This opens up the challenging question, why looking for a relationship with an entity that itself depends on temperature rather than going the direct way. If there is a simple proportionality between temperature and volume without singularity and without further temperature-dependent processes that take place simultaneously, the answer should be: the introduction of volume is unnecessary. However, fact is, such a simple proportionality does not exist in reality. Already the simultaneous temperature dependent development of vapor pressure which takes influence on the distribution of internal energy, questions a simple proportionality. Looking back onto the model it should be evident that, at least, there are two different processes increasing volume with temperature, at first the normal thermal expansion as common also for crystalline matter and, in the case of liquids, the generation of additional volume by the aforementioned process (see fig. 3). Both partial volumes do not necessarily exhibit the same temperature dependence. Consequently, the situation could be formulated in such a way that the energetic framework conditions are concealed in the development of the volume (and vapor pressure) and are not necessarily to be considered for subsequent derivative relationships. Therefore, the introduction of volume into an equation describing the dependency of transport properties on temperature seems to be obligatory, and the definition of free volume is of great importance, not least with regard to the influence of pressure, the third main variable of the two-phase system.

Defining the Boundary Line between Liquid and Glass

Definitions of Free Volume

At first glance, the term "free volume" appears to be quite plausible. However, in literature the definitions of "free volume" are very different. Definitions and correlations can be found that are either based on the basic molecular volume ΣV_M , the liquid volume V_l extrapolated to 0 K (Doolittle⁶⁷) or the crystalline state. In the diagram below (fig. 3) V_K is shown as a definition that defines the volume at the Kauzmann temperature T_K , the temperature at which the extrapolated curve of the equilibrium density of the liquid intersects with that of the crystalline state, as basic volume. As this volume according to the new model cannot be reached by a glass consisting of non-spherical elements but only in an ordered crystalline state this definition is regarded as irrelevant, same as the reference to V_{k_0} . The definition $V_{f_{hs}}$ which is based on the molecular basic volume ΣV_M (Van der Waals volume, hard sphere volume) may not be used for defining free volume as it implies the configurative volume V_{conf} . The configurative empty space V_{conf} as difference between the zero point volume $V_{g_{00}}$ and the molecular volume ΣV_M is determined by the molecule shape and cannot be further reduced. Even at higher temperatures, it has to be assumed that part of the space which is not occupied by molecules, cannot be used by neighbor molecules for position changes due to its too small dimension. The free volume according to V_{sw} ⁶⁸ should have no direct relation to the viscosity.

Fig. 3 demonstrates some possibilities to define the free volume.

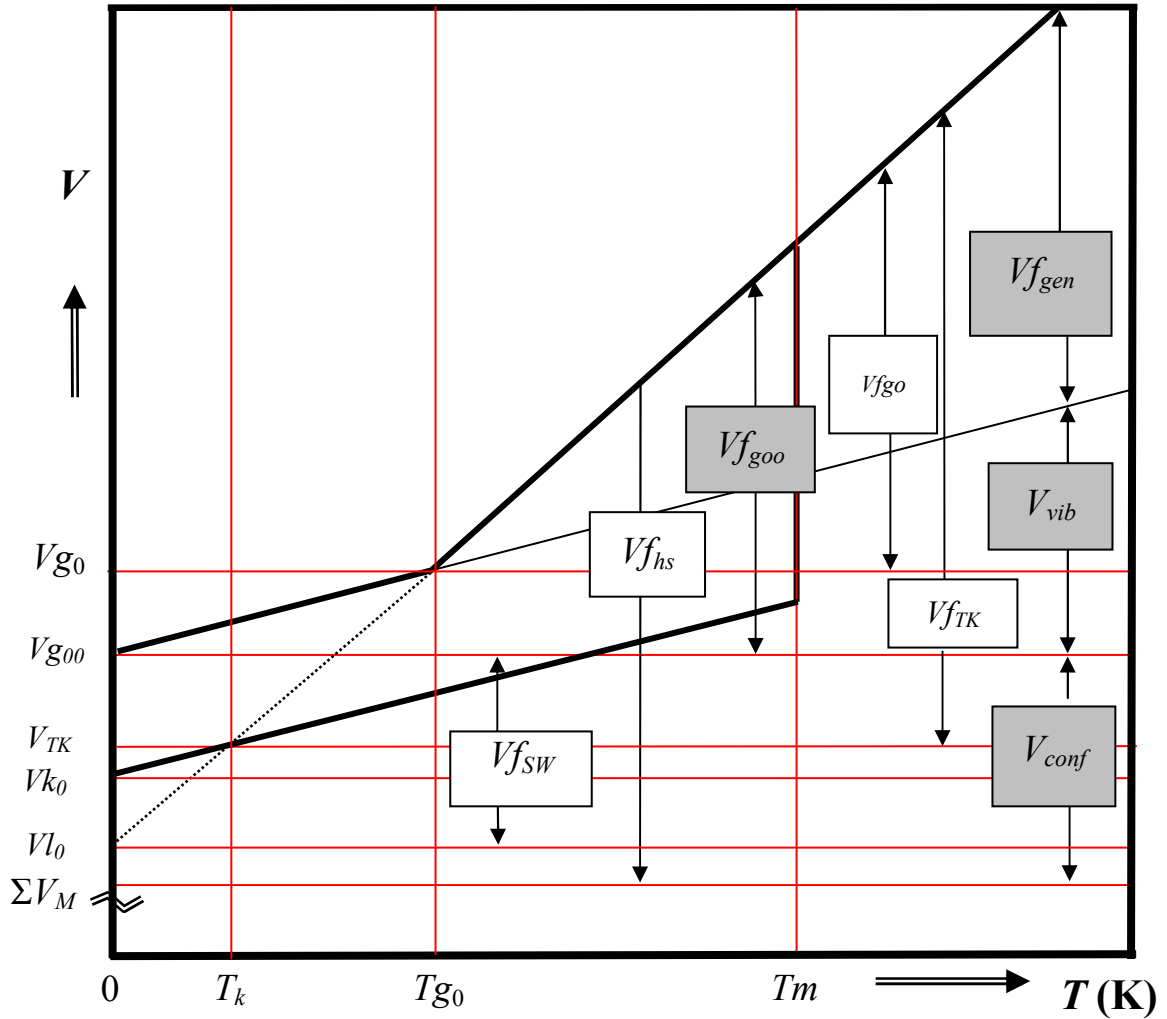


Fig. 3 Possibilities to define free volume

(To simplify things, the graphic does not consider the influence of the possibilities of axis orientation and vapor pressure)

According to figure 3, the specific volume is therefore composed as follows.

$$V_{(T)} = \Sigma V_M + V_{conf} + V_{vib(T)} + V_{gen(T)} \quad (1)$$

This definition does not take into account the influence of the pressure, which should also have a large or very small influence on the temperature-independent partial volumes.

How free volume should be defined depends on the fact whether or not one considers the vibratory expansion at T_g , $V_{vib(g)}$ as free volume being useable for transport processes and whether one considers a basic volume necessary.

Below three differently defined “free” volumes will be discussed. One case implies different viscosity behavior at the limits of the liquid state.

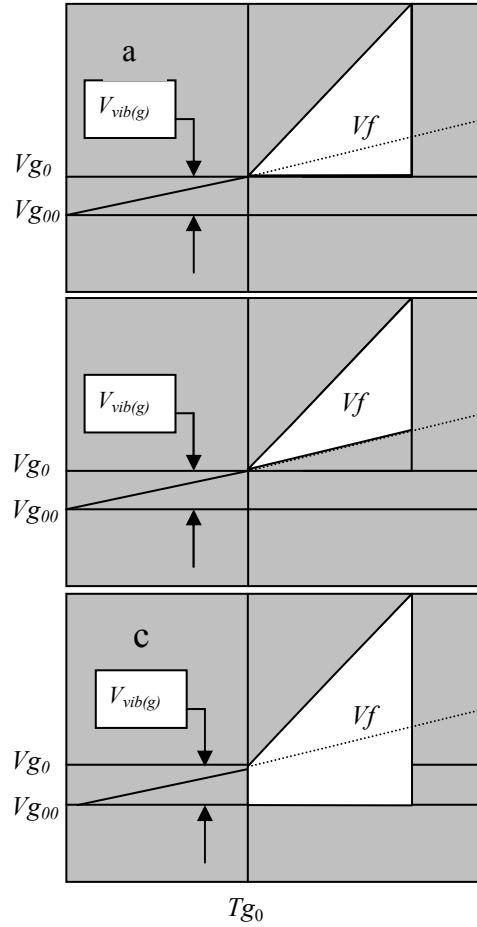


Fig. 4a-c Possible Definitions of free volume

In the case shown in Fig. 4a, the free volume is generated above Tg_0 respectively Vg_0 . It includes the additionally generated volume and that part of the vibration expansion volume above Tg_0 .

$$\begin{aligned} Vf &= V - Vg_0 \\ \lim T(\eta \rightarrow \infty) &= Tg_0 \\ \lim V(\eta \rightarrow \infty) &= Vg_0 \end{aligned}$$

Fig. 4b assumes that only the newly generated volume V_{gen} is available for transport processes.

$$\begin{aligned} Vf &= V - V_{vib} - Vg_{00} = V - Vg_0 - (V_{vib} - V_{vib(g)}) = V_{gen} \\ \lim T(\eta \rightarrow \infty) &= Tg_0 \\ \lim V(\eta \rightarrow \infty) &= Vg_0 \end{aligned}$$

In fig. 4c the total vibration expansion volume suddenly becomes useable free volume at Tg .

$$\begin{aligned} Vf &= V - Vg_{00} = V - Vg_0 + V_{vib(g)} \\ \lim T(\eta = \eta_{max}) &= Tg_0 \\ \lim V(\eta = \eta_{max}) &= Vg_0 \end{aligned}$$

In previous studies by the author the vibratory expansion volume V_{vib} was also considered inaccessible volume for translation processes. However, if the entire molecule matrix vibrates within in itself, it should be impossible to distinguish between V_{vib} and additionally generated free volume V_{gen} . A separate question is, do both sub-volumes regulate the change in viscosity when temperature changes or only V_{gen} ? A good argument is that V_{vib} also influences viscosity, possibly as an ‘‘Arrhenius contribution’’. In the numerical analyses (s. part II) it is convincingly shown for simple molecular liquids above T_m that free volume corresponds to $V-V_{g_l}$, whereby V_{g_l} replaces V_{g_0} in fig. 4a. (To the definition of V_{g_l} see later)

In literature sometimes the expression ‘‘getting deeper into the state of the glass’’ is used. That phrase is based on the idea that suitable measures can be taken to approach the Kauzmann temperature or at least the Vogel temperature or the temperature T_2 of the ADM theory⁷. As already mentioned, this is not possible with irregularly aligned molecular axes, but the path below T_{g_0} would only be possible with at least partly parallel aligned axes. If the intersection point at T_2 or T_k would exist, then this implies that the vibrating elements have to be arranged in a spatial alignment of the molecular axes at decreasing temperature, which would then be identical to the crystalline state at their intersection point. This scenario does not seem to make much sense in view of the increasing mutual obstruction and extremely small free volume. Spherical molecules such as noble gases are an exception due to their uniform axes, as already mentioned. Figure 5 shows the time-dependent development of the specific volume at constant cooling rate.

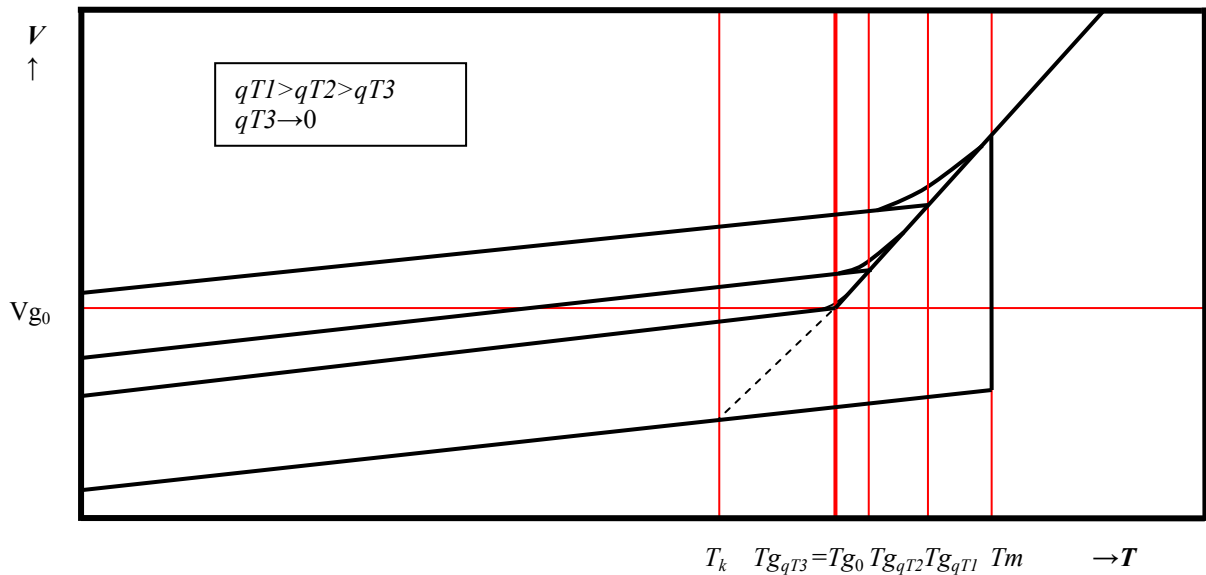


Fig. 5 Time-dependent development of specific volume (schematic)

$qT1$, $qT2$ and $qT3$ are three different cooling rates, the first being the fastest. With $qT3$ the rate approaches zero and $T_{g_{qT \rightarrow 0}} = T_{g_0}$. With T_{g_0} , the lowest achievable specific volume V_{g_0} is reached for a completely disordered material. The path along the dotted line in the direction to T_k is not feasible with unaligned molecular axes but only in the (partially) crystalline state.

Influence of axis orientation in space

Temperature dependent generation of empty spaces and time dependent axis orientation are in principle two different processes. In the very high temperature range the vibration amplitudes are large and the free spaces generated by combined actions are big enough to become occupied by all neighboring elements independently of their axis orientation in space, only governed by the appropriate direction of modes. That range should be the normal low-viscosity region. Decreasing the

temperature to T_{g_l} all apertures become smaller than the largest molecular diameter of the vibrating molecules. This means axis orientation in space starts to get influence to translational possibilities. The number of position changes decreases stronger than it would happen without alignment restriction because translations are only possible when the axis of an element is aligned in space such that the projection onto the gap is smaller than its diameter. Lowering the temperature further finally leads to a situation where the broadest apertures of the void distribution only allow vibrating elements to translate when their cross-sections, totally or partially, are smaller than the diameter of that aperture and, additionally, are pointed to the gap. The limit volume of the liquid state is reached in this situation and can be termed V_{g_0} . Since at T_{g_0} about half of the distribution width of the vibration amplitudes corresponds to a $V > V_{g_0}$, a limited flowability is still present at T_{g_0} . Only when the temperature is lowered further to T_{g_g} are all openings at V_{g_g} smaller than the smallest molecular cross section, so that passageways become impossible. Then the disordered solid state should be reached. Figure 6 shows the relationships outlined above:

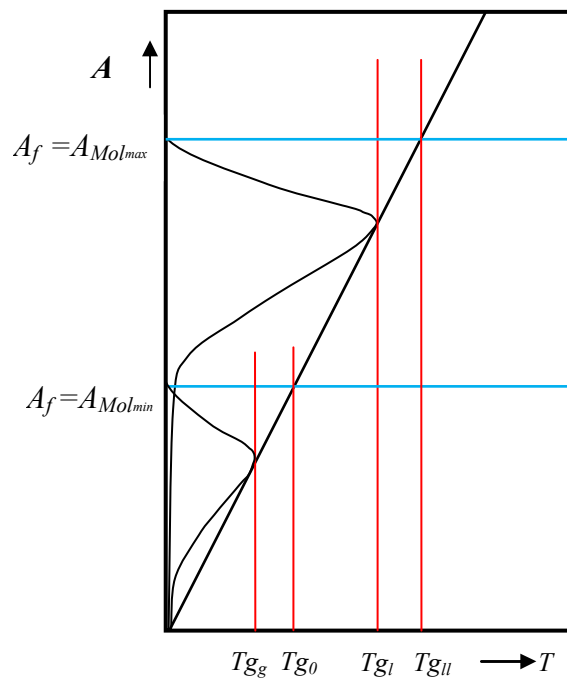


Fig. 6 Limitations of viscosity regimes (schematic)

The ordinate of fig. 6 exhibits the size of the cross-sectional area of the temperature depending gaps A_f . The blue lines represent the cross-sectional area of the smallest and the biggest molecular axes. The curved lines symbolize the distribution width of gaps for one distinct temperature characterized by the maximum of curves. For $T < T_{g_g}$ all gaps are smaller than $A_{Mol_{min}}$, the cross-sectional area of the smallest molecular part, so no translational movement is any longer possible. Below T_{g_g} there is only the solid glass. Above $T_{g_{ll}}$ the pure liquid state is reached. The upper limit $T_{g_{liq}}$ of the smallest molecular axes was not drawn for reasons of clarity.

In practice the ideal glass state without any usable free volume cannot be reached by normal cooling because of too long waiting times for the molecular rearrangement.

Certainly, there is empty space in between the molecules also below T_{g_0} , but that volume (*configurative empty space* V_{conf}) cannot be filled with adjoining molecules or parts of them due to too small dimensions.

Undoubtedly, changes in position below V_{g_0} or T_{g_0} are much less frequent than above, since three states must occur simultaneously:

- a gap must be wider than the cross-section of the smallest dimensional portion of a neighboring molecule
- the alignment in space of the molecular axis of an adjoining molecule must be pointed to the gap
- and, last but not least, the direction of the mode of that vibrating molecule must be strictly directed to the aperture.

Therefore, the influence to transport properties should adopt a new quality and the interesting question comes up whether there are differences between the various classes of material. It should be clear that chain molecules are not able to shift entirely, whereas non-spherical simple molecules have more than one possibility to move through a neighboring opening. As the numerical analysis of simple molecular liquids shows, T_{g_l} corresponds to the temperature at which the viscosity appears to diverge. In reality this is not the case as fluidity persists until T_{g_0} (resp. T_{g_g}) is reached. This partition between two viscosity regimes has also been addressed by mode coupling models as “dynamic cross-over”. In fact, the characteristic temperature T_c of these models corresponds approximately to T_{g_l} (deducted from V_{g_l}). On the other hand, however, only side-groups or segments of chain molecules can shift through an adjacent aperture so that the viscous behavior corresponds to the simple molecules below V_{g_l} . Therefore, with chain molecules V_{g_l} does not intervene and only V_{g_0} controls the viscosity. This statement was convincingly verified with viscosity data of polystyrene and polybutene whereby viscosities at a T/T_g -relation of 1.08 were included into the regression analysis without any kink in the viscosity curve being visible..

Corresponding to the model spherical molecules should not change their behavior at a certain V_{g_l} . That implies viscosity obeys only one functional relation with decreasing temperature. Assuming that there is only one driving force that causes the molecules to adopt the equilibrium positions with the lowest free energy, the spatial arrangement of spherical molecules at the glass transition should not deviate from the arrangement in a densely packed crystal. If this assessment holds, a glass formed at a temperature T_x below T_m should have the same density and structure as the crystal formed at T_m at the same temperature. In the case of spherical molecules, therefore, no distinction should be possible between glass and crystal. Part II confirms this important statement using the example of noble gases. (Argon: $V_{cryst.}$ 0.619 gcm^{-3} - from viscosity calculations $V_{g_l}=V_{g_0}$ 0.616 – 0.622 gcm^{-3} ; Krypton: $V_{cryst.}$ 0.334 V_{g_0} 0.34-0.35; Xenon: $V_{cryst.}$ 0.274 V_{g_0} 0.27; Neon: $V_{cryst.}$ 0.66 V_{g_0} 0.72-0.74).

For non-spherical molecules, on the other hand, the difference between T_{g_0} and T_{g_l} is expected to depend on the ratio of A_{Molmax} to A_{Molmin} (s. fig. 6).

Pre-Crystallizing and Supercooling

Deducted from the course of viscosity temperature dependence of simple liquids in both regions, above and below T_m , a cross-over of different molecular transport mechanisms in two temperature regimes was concluded in 1965 by Barlow, Lamb and Matheson³¹.

The author in his 1980/1981 studies^{69, 70} depicted the viscosities of o-terphenyl, the salt blend potassium nitrate /calcium nitrate 60/40, glycerol and those of the glass standard of the German glass society as $\log(\eta) = f(\log(1-T_g/T))$ and demonstrated the different behavior, too. The two of them first-mentioned showed a distinct kink at a certain temperature which was interpreted as a change in packing density in connection with pre-crystallization appearing in the vicinity of the melting point.

As the molecular distance can be shorter with uniform alignment of molecular axes (crystalline state) than with axes pointing into all directions of space (glassy state) the system prefers the crystalline state and tries to reach it by partial rotations. That should be principally valid for all temperature regions. Because of the temporally and spatially fluctuating input of thermal energy into the system, at higher

temperatures, however, axis alignment is disturbed and prevented. Only when local thermal energy and cohesion energy are in equilibrium can regions with increasingly oriented axes (pre-crystalline regions) form. This structural change cannot remain without affecting the transport properties. As the temperature gradually decreases, these areas increase and form nuclei to which further molecules attach quickly, which eventually leads to an immediate crystalline solidification. If, on the other hand, cooling takes place very quickly, enlargement of the pre-crystalline zones is impeded and no nuclei can be formed or at least no crystallization can take place. Similar considerations are taken up again in the 2004 work of Blazhnov et al.⁷¹, although the role of nuclei seems somewhat over-emphasized and the negation of influence on viscosity may be questioned. Dyre⁷² assumes “fairly large and well-defined crystallites” which are deformed and hardly detectable by standard X-ray or neutron scattering. Semmelhack and Esquinazi⁷³ investigated “metastable ordered structures” and “unstable crystalline structures” in OTP.

In this context, the conditions of physical vacuum deposition (PVD)^{74, 75, 76} must also be addressed. During this process, monomolecular layers are successively deposited from the gas phase onto a substrate that has a temperature below the conventional glass temperature T_g (DSC $qT=10$ min/K). Depending on the substrate temperature, denser or less dense glasses are obtained than those with conventional cooling. The process is used, among other things, to “get deeper into the glass state and to achieve more stable glasses”. It should be remembered that a glass must by definition have a completely disordered state. Each partial order leads to a nearer approach to the crystalline state and thus to higher densities. However, such a partial order is to be expected with the PVD, because there is a high probability that the molecules will not be arranged with the longest axis vertically on the substrate. Compared to the glasses obtained conventionally from the liquid by cooling there should be a lack of one spatial component in the precipitated glasses. PVD-glasses should correspond to an intermediate stage between the completely amorphous and the crystalline state. Therefore, PVD results cannot easily be compared with conventionally obtained results.

As already known from the 1965 work of Barlow, Lamb and Matheson³¹ the viscosity behavior of some simple liquids at the region of the melting point of the crystalline phase changes without visible crystallization and barely perceptible variances in density. Therefore, one can start from the premise that with simple liquids approaching T_m a pre-crystalline state successively will be generated and that, considered physical, there are two different substances above and below the melting point.

A coherent equation of the viscosity behavior encompassing both regions with common parameters should therefore be inadmissible. This does not mean that no composite equation could be developed to describe the whole range, although it should be strongly assumed, that the properties in the supercooled region are depending on the measuring and cooling conditions.

An interesting question regards the assignment of T_g to the crystallization behavior. In the suggested model, the change in viscosity behavior is also connected to the spatial alignment of the molecular axes. Indeed, it seems that a connection exists, whereby T_g in most cases is situated some temperature degrees below T_m , possibly in the region of maximum crystallization rate. The problem will further be addressed in part II of this work.

Glass Transition/Transformation Range

Using the usual methods of measuring glass (transition, transformation) temperature, dilatometric or calorimetric measurements with constant rate of change in temperature $qT=\pm dT/dt$, depending on it, the molecular elements do not have enough time to maintain equilibrium density below a certain temperature. The temperature range in which this time dependence is clearly perceivable is defined as transformation or glass transition range, the deviation from equilibrium density as “beginning

freezing". It has to be pointed out, however, that the width of the "transformation range" is variable depending on qT and can be moved on the temperature axis. This is also true for the hysteresis range used for definition purposes by Mazurin and Rekhson⁷⁷. Theoretically, there is no upper limit since the thermodynamic equilibrium is fundamentally disturbed when the rate of temperature alteration is higher than the respective relaxation time of the inner structure. The fictive temperature T_f , i. e. the temperature that the system would have in equilibrium with the current density, deviates the more from the current temperature the faster the cooling rate or the higher the relaxation time of the inner structure respectively the higher the viscosity is. In the sense of the presented model concept, the volume deviation from the equilibrium density is not interpreted as a beginning freezing. As long as the actual temperature remains above the true glass temperature T_{g_0} during the cooling process, i. e. that temperature at which V corresponds to V_{g_0} , the system tries to achieve the equilibrium density and will finally reach it after sufficient waiting time. Therefore, the "glass transformation", in that inadequate sense, would be not a special property of supercooled liquids but in general that of any liquid which is being cooled from any high temperature. To put it in a nutshell, starting at a very high temperature with a fast cooling rate the fictive temperature T_f , and thus density, may deviate from the equilibrium density even above T_m .

Another question arises, what happens when the temperature of the out-of-equilibrium-liquid falls below T_{g_0} . Then we get the scenario that small vibratory amplitudes are coupled with an excessive empty space. The fact that within the range close to T_{g_0} many properties depend not only on temperature but also on time was emphasized by Williams, Landel and Ferry²⁸ which established for this range their well known time-temperature superposition principle. In order to use the WLF equation it is not necessary to know T_{g_0} but one may use an arbitrary temperature parameter within wide bounds. This underlines the above assessment that the deviation from equilibrium density is only indirectly related to glass formation.

The topic of excess free volume is of great practical importance, for example, for the ageing of polymers. It has been studied in the context of the fictive temperature concept by many researchers (f. e. ^{78, 79, 80, 81, 82}) and falls outside the scope of this work, but the model presented here can also contribute to a changed perspective. The basic principle should be that an ideal glass, i. e. a glass without free volume, should not be subject to physical ageing.

Only below T_{g_0} , the temperature at which the apertures produced are smaller than the smallest cross-section of the elements and $V < V_{g_0}$, should a material be termed "glass", either as an ideal glass or as a real glass, which still contains some free volume, as it is the only achievable case. An ideal glass does not contain free volume available for transport processes and, therefore, it should be a stable matter. Whether the ideal glass state, should be called a metastable state in thermodynamic terminology, is a question of definition. As the undirected molecular axes prevent the molecular centers to position themselves to the potential minima, there should be an "adaptive power" which, however, cannot be effective. From this point of view the terminus "metastable" should be appropriate. Nevertheless there remains certain arbitrariness because a lot of substances are able to crystallize in more than one form with different densities and they are all defined as stable in the thermodynamic sense.

In his 1991 work, Angell emphasized the thermodynamic importance of T_0 in the VFT equation by comparing the ratios of T_g/T_0 and T_g/T_k , which are the same for some substances where entropy was measured below T_g . However, this assessment does not call into question the fact that the glass transition at T_{g_0} interferes and the alignment of the axes becomes impossible. Nevertheless, the assessment has a physical significance with spherical molecules, as said. T_{g_0} (derived from V_{g_0}) and T_k should be the same if the alignment of the axes in the liquid and the crystalline state are identical.

A further question arises in regard to the classification of glass transformation in the thermodynamic sense. There are different counts of freedom above and below V_{g_0} , but the vibratory behavior does not

change when passing T_{g_0} . Doubts remain also as to whether the production of *additional* empty volume would mean the formation of a new phase. It seems to be problematic to speak of two phases. However, it should be quite legitimate to speak of two different states of aggregation, whereby the author would prefer the term "glass transition" in comparison to "glass transformation" because the latter term would mean the transformation of one form into another, whereby the term "form" is more associated in terms of shape than for different aggregate states.

Identifying T_{g_0} from measurements

Since the definition of T_{g_0} is one of the key questions of the whole topic of glass formation, it seems necessary to give a brief overview of the methods for determining the boundary between liquid and glass. The measured T_g value is not a constant value as is well known, but depends on qT and should usually be marked with a suffix. The tangential inclination of the liquid side of the DSC-transition step should be a function of the volume viscosity and the deviation from the thermal equilibrium. The latter is very different for different substances at the same distance to T_{g_0} , since it is very likely that the molecular packing density also determines the inclination. Consequently, the physical importance of $T_{g(qT>0)}$ is thereby restricted. Incidentally, the detected time dependence is not limited to T_g only. DSC measurements of crystalline matter show a temporal dependence of the same order for the beginning of crystallization⁸³ (Fig. 3b there).

As the molecular vibrations are not uniform but distributed around a center value, the glass transition should not take place as singularity but in an interval. This should be valid independently from the preset cooling or heating rate, even for $qT \rightarrow 0$.

From dilatometric measurements the onset of the glass transformation T_{g_g} may be taken as that temperature at which an initial alteration of the expansion coefficient in the glassy state is perceived. The fact that in spite of different temperature changing rates the coefficients of volume expansion retain a constant value at a given characteristic temperature for the glass has been proven by studies of Bero and Plazek⁸⁴ on an epoxy resin.

The phenomenon is, however, already to be seen in former volume curves, e. g. by Ritland⁸⁵ for a BSC glass, Rötger⁸⁶ for the glass "Jena Normal 16 III", deBolt et al.⁸⁷ for B_2O_3 and Chen and Turnbull⁶⁴ for a gold-germanium-silicon-alloy.

That the sight from the glass side is the correct one to evaluate T_{g_0} has been also confirmed by dielectric studies. For toluene Döb et al.⁸⁸ have demonstrated that the dielectric constant independently from the used measuring frequencies always show a sharp kink at $T = 117K$, the same value as measured by DSC. (s. fig. 1 of that paper). Another impressive confirmation may be drawn from fig. 3 for a basaltic melt in Yue et al.⁸⁹

If T_g is defined thermo-analytically (DTA, DSC), then T_{g_g} is that temperature at which the basis line turns upward for the first time during the heating process. Exemplary measurement results are given there for instance in fig. 3 for $CH_3COO(Li_{0.86}Na_{0.14})$ (T_{g_g} approx. 360K) and in fig. 6 for GeO_2 (T_{g_g} approx. 740K) in the study by Brüning and Crowell⁹⁰.

Fig. 7a below uses the change of heat capacity in the transformation range to give an example of the typical course at fixed cooling rate and variable heating rate.

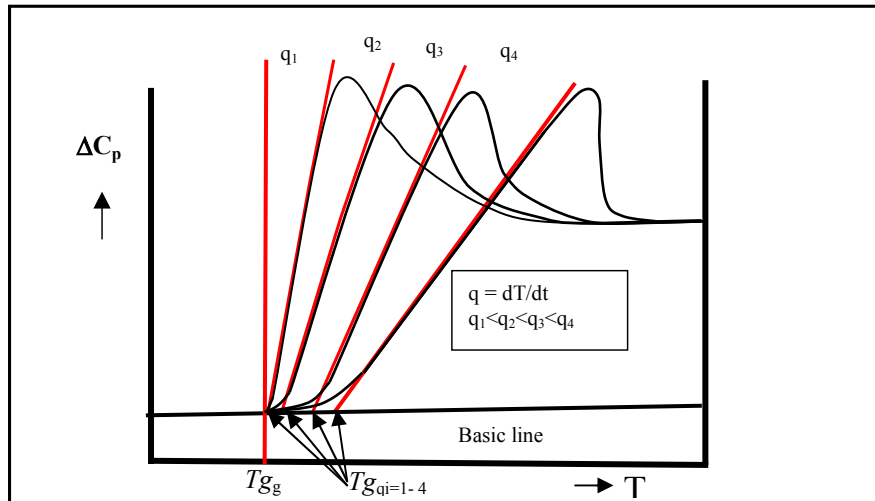


Fig. 7a C_p -leap at T_g (schematic) – Typical DSC scans with fixed cooling rate and variable heating rate.

The higher the heating rate the flatter the curve turns from the basis line, the turn occurs, however, always at T_g . (For $q_1 \rightarrow 0$ $T_{g_{q_i=1}}$ will become T_g . T_{g_0} is then situated nearly midway on the flank, see later). The curve peaks are overshoots and all curves merge at higher temperatures to the same c_p -value. The width of the T_g -interval is different and depends on the cooling rate.

As shown in fig. 7a, the $T_{g_{q_i}}$ values depend on the flank's inclination of the C_p step. The apparent dependence of T_g on the temperature alteration rate represents the basis for many theoretic discussions and, therefore, is of vital importance for the understanding of glass transition. It shall again be pointed out that, following the model outlined above, there is no immediate function $T_{g_0} = f(qT)$. On the contrary $T_{g(qT)}$ depends on the distance to T_{g_0} and presumably on packing density. The tangent's inclination is determined by the relation qT/τ and since the relaxation time τ apparently tends for $T \rightarrow T_g$ towards ∞ , the change of the inclination angle also should converge asymptotically to the inclination for $qT \rightarrow 0$. That there is a final inclination for $qT \rightarrow 0$ should not only bear upon the practice of measuring T_g , but it is also of theoretic importance for the implications of mode distribution in the transition interval.

DSC scans with a fixed heating rate and variable cooling rate result in an uniform $c_p(T)$ curve, which only differs in the overshoots.^{91, 92}

Fig. 7b shows scans with fixed heating rate and variable cooling rates.

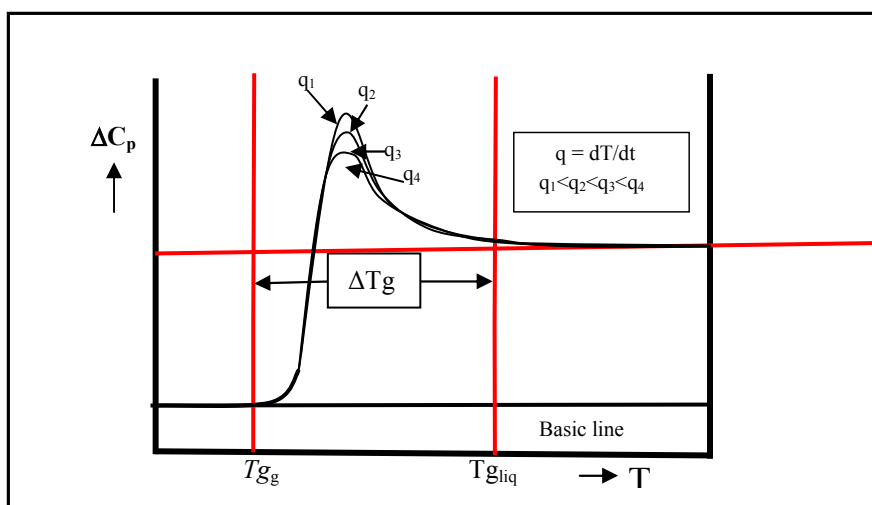


Fig. 7b DSC-scan with fixed heating rate and variable cooling rates (schematic)

The scans in Figure 7b give a uniform curve flank on the low temperature side for all cooling rates, also for $qT \rightarrow 0$. However, the position of the flank on the temperature axis depends on the heating rate, so that Tg_0 cannot be determined. Tg_0 , on the other hand, depends additionally on the slope of the flank, which in turn depends on fragility, to put it in Angell's terminology. Therefore, Tg_g was chosen as the lower limit value, i. e. the temperature under which the pure glass state is present and the first change in the curve is clearly visible.

In the literature one often finds representations of $Tg_{(qi)}$ as a straight line plotted over $\log(qT)$, and indeed with the usual qT values, this relationship seems to be valid with many substances from different material classes.

$$Tg_{(qT)} = Tg_{(qT=1)} + u \cdot \ln(|qT|) \quad (2)$$

Such plots give the impression that there is no Tg_0 . However, the equation does not rule out that there is a cooling rate qT_{min} , falling below of which has no more effect on the overall system.

With qT_{min} , the limit state is reached at which the transition from the status "solid particles in liquid medium" to "droplets in solid medium" takes place (see section "Influence of mode distribution approaching Tg_0 ").

Exemplary results are shown by the dilatometric studies of Bero and Plazek⁸⁴ and the work of Brüning and Crowell⁹⁰ using DSC-results of LiNaAcetate and GeO₂, Greiner and Schwarzl⁹³ and Hadač et al.⁹⁴

The dilatometric results of an epoxy resin used by Bero and Plazek⁸⁴ are very interesting because they were obtained at very low cooling rates. Therefore, they should be analyzed in more detail.

Depending on the cooling rate qT_i , the following Tg_i values were measured:

Tab. 1 Dilatometric Results for Epon 1001f-DDS

qT (K/min)	Tg_i (K)
0.9	131.7
0.25	130.5
0.05	128.9
0.003	126.1

The first deviation from the expansion coefficient of the glass was detected above $Tg_g = 118$ K.

Using equation (2) the following equation parameters are obtained:

$$Tg_{(qT=1K/min)} = 131.83 \text{ K}; u = 0.9847$$

If table 1 is extended with Tg_g and the standard deviation is determined as a function of an arbitrarily assumed effective minimum cooling rate, the following regression results are obtained:

Tab. 2 Evolution of standard deviation with arbitrarily chosen qT_{min} for Epon 1001f-DDS

qT_{min} (K/min)	$\sigma(Tg)$ (K)
1E-009	0.86
1E-008	0.64
1E-007	0.35
1E-006	0.054
9E-007	0.038
8E-007	0.028
7.95E-007	0.0278
7.5E-007	0.0297
7E-007	0.037
5E-007	0.091
1E-005	0.607

Figure 8 shows the steep but finite increase in the gradient of $Tg(qT)$ at very slow temperature changes.

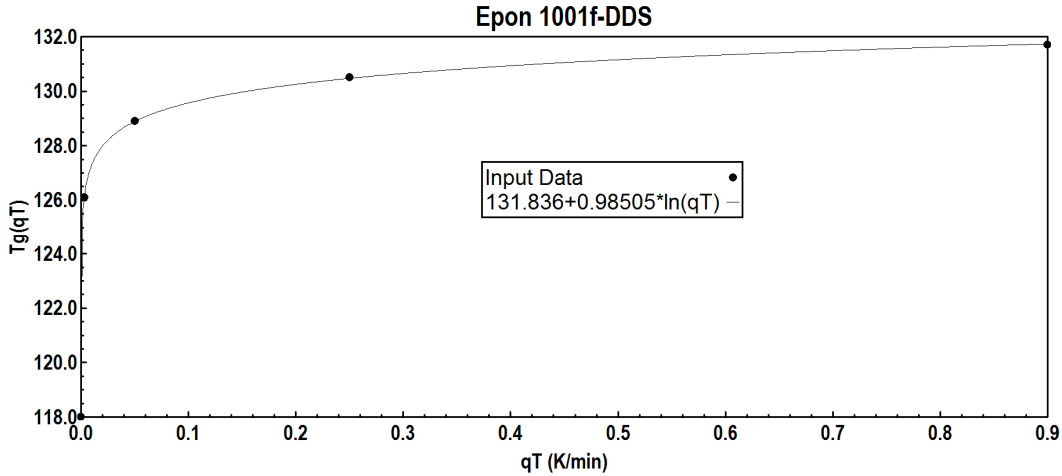


Fig. 8 Development of $Tg(qT)$ with $qT_{min}=7.95E-007$ ($r^2=0.999981$; $\sigma=0.028$ K; $\Delta_{max}=0.032$ K)

The surprising idea that a certain qT_{min} should exist was first stated by Bero and Plazek⁸⁴ in their work of 1991:

“The data indicate that upon sufficiently slow cooling (ca. 2°C per Century) a sharp transition should be observed which could be thermodynamic in nature, since Tg would be independent of rate at all slower rates.”

These authors state furthermore:

“If the data correctly indicate bona fide evidence for a Tg-related thermodynamic transition, it does not seem likely that it is the T_∞ suggested by a free volume analysis, or the T_2 of Gibbs, Adams, and Dimarzio, since the observed constant temperature of 118 is but 14°C below the Tg obtained at a rate of cooling of 0.9°C/min. The values of T_∞ and T_2 are usually thought to be some 30 to 60°C below the nominal Tg obtained at about a 1°C/min rate of cooling.”

An interesting result offers the comparison of the qT_{min} -Parameter for EP with the stated value of Bero and Plazek: 2K/Century = $2.6 \cdot 10^{-7}$ K/min versus $7.9 \cdot 10^{-7}$ K/min. Bero and Plazek gave no derivation for the stated value but it can be supposed that it is surely not pure invention. In any case, it is a remarkable agreement.

Influence of Mode Distribution Approaching Tg_0

Two very principle questions remain: Which influences could cause fixing of liquid structure when the cooling rate falls down qT_{min} , and does viscosity really get to infinity when approaching Tg_0 , as figs. 4a and 4b imply? Which role plays mode distribution in the scenario?

This leads to the influence of the vibration amplitudes in the transformation interval and will be examined now. The vibrations of the vibrating elements are undoubtedly distributed around a mean value corresponding to the respective temperature. The width of the vibration amplitudes is limited and corresponds to a defined range of specific volumes V_i . Vg_0 represents the specific volume below which the openings between molecules are smaller than the smallest molecular axis cross sections. If, when approaching Vg_0 , the lowest V_i -values within a distribution are smaller than Vg_0 , the result is a state in which both liquid and solid matter is present. This state exists principally in the glass transition interval between Tg_g and Tg_{liq} .

The relations in the transition interval are depicted in fig. 9

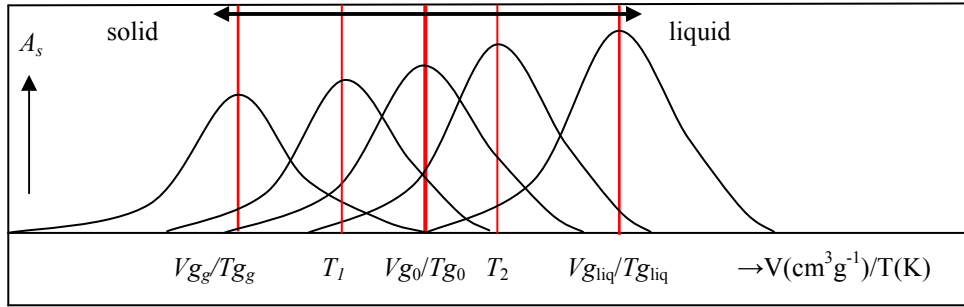


Fig. 9 Influence of the vibration width at a chosen specific temperature

At T_{g_g} the vibration width respectively all V_i are smaller than V_{g_0} . The solid state is given. When the temperature is raised to T_1 , some V_i exceed V_{g_0} and the total system consists of a solid matrix surrounding liquid droplets. At T_{g_0} , about half of the total system (see section “Location of T_{g_0} in the transition interval”) is solid and the other half liquid. At the temperature T_2 , the system consists mainly of the liquid phase, which contains a proportion of solid particles. At $T_{g_{liq}}$ the system is pure liquid, because no single V_i is lower than V_{g_0} . (A_s are the vibration amplitudes)

In connection with qT_{min} the range between T_{g_g} and $T_{g_{liq}}$ will become of special interest. Below $T_{g_{liq}}$ more and more solid glassy matter will be formed and it is assumed that there exists a suspension-like state. Decreasing the temperature furthermore there should be reached a state where the solid predominates and starts building a fixed structure with enclosed liquid droplets. That state should not be able to relax furthermore and qT should not have any longer influence to viscosity. That limiting qT should be the above stated qT_{min} . (s. a. in this connection: Zondervan et al. 2008⁹⁵). Of course, the included liquid droplets become smaller and smaller and can continue to relax, but this can no longer affect the entire system. Therefore, in accordance with the fixed relaxation time at that point viscosity should attain its maximum equilibrium value.

Kobayashi et al.⁹⁶ using a new method of viscosity measurement on polystyrene showed that the slope of viscosity plotted over temperature exhibits an inflection point approaching T_g and supposed a crossover to Arrhenius behavior. In part II of this work it will be shown on the example of supercooled 6-phenylether that a viscosity-temperature relation which includes a finite maximum value at T_{g_g} yields superior results compared to equations with infinite viscosity at a distinct low temperature or to equations without any singularity. Part III will deal especially with supercooled liquids and the problems there.

Already published are results of

OTP

(DOI 10.13140/RG.2.1.1244.5209)

B2O3; CKN 60/40; 3-NAB; 2-Methylpentane

(DOI 10.13140/RG.2.1.3387.6244)

Albite; Anorthite; Diopside

(DOI 10.13140/RG.2.1.4349.4166)

Finally, the different states including the influence of T_m and axis orientation shall be illustrated in Fig. 10.

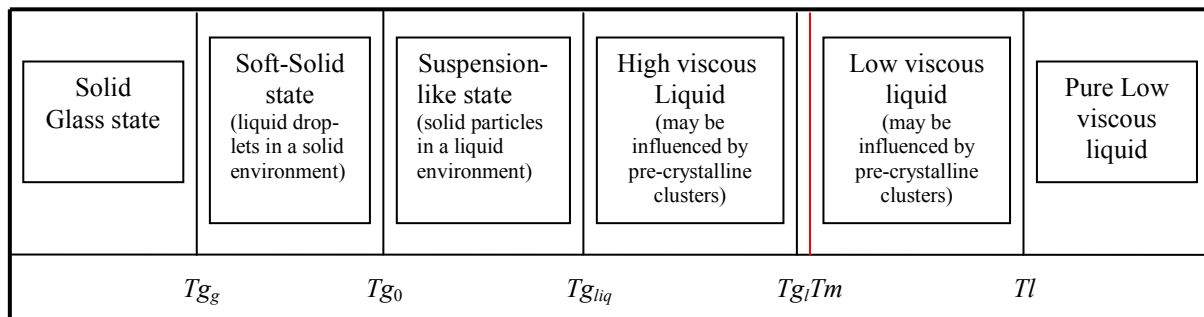


Fig. 10 State limitations

Location of Tg_0 in the transition interval

Another interesting question refers to the limits and mean values of mode distribution in the transition interval. In the study of Holubová et al.⁹⁷ the Step Scan DSC technique had been applied. The authors point out that the ascertained Tg values are independent from thermal history and rate of temperature change. For various substances with Tg values in between 23°C and 507°C the transformation intervals were determined. The authors conclude from the gathered data that the glass transition cannot be seen as a pure kinetic process. They propose to define the inflection point determined by the Step scan-DSC technique as clear material specific glass temperature.

If one presupposes that real matters show a vibration distribution around a medium value, the C_p step, as set out above, has to show an inclination and to cover a temperature interval even with the cooling rate decreasing towards 0. Consequently, the selection of the inflection point within the interval seems to be absolutely reasonable. At normal DSC measurements this inflection point is, however, not visible as it is covered up by the time depending enthalpy modifications. In that case, it remains reasonable to define the first deviation from the basis line as Tg_g .

In the study dated 2003 (Holubová et al. op. cit.⁹⁷) the inflection point T_i was fixed at 0,632 of the entire interval width. In a later study (Chromčíková et al.⁹⁸) the position of the inflection point was stated as $0.5 \cdot RT_i / \Delta H$. If one considers the vibration distributions being deemed qualitatively possible for the limit temperatures of both states, and if one supposes that the distribution width is in proportion to the respective temperature, it may be suggested that the inflection point is situated in the lower interval region close to the centre value in accordance with the a.m. study. In the second part of this thesis it will be shown that the best results of the calculation of viscosity when approaching the glass transition interval are obtained when $\Omega = e^{-\Omega} = 0.56714$ is selected as inflection point. By choosing Ω , the viscosity reaches its maximum value and $d\eta/dT$ becomes 0.

Finally, it should be pointed out how much the width of the transition interval can differ in the different substance classes. If one puts the distribution of the vibration amplitudes in proportion to the density fluctuation, the relation between the limiting and the medium temperatures is well clarified as shown in fig. 11.

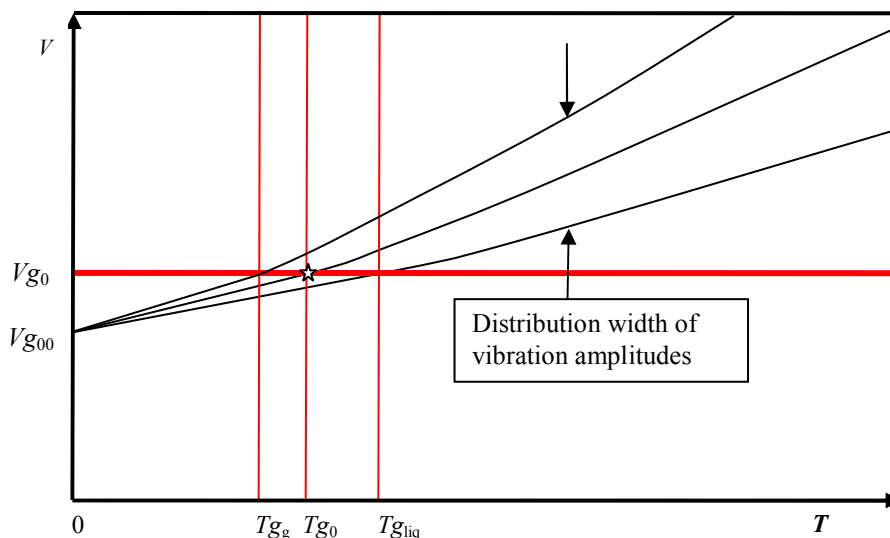


Fig. 11 Width of the transformation interval in dependence of the magnitude of Tg_0 (schematic).

The crucial quantity is V_{g_0} , since it is connected with the molecule size and geometry.

From fig. 11 a feature of highly practical importance may be deduced. The width of the transformation interval depends strongly on Tg_0 itself, roughly as a rule of thumb about $0.1 Tg_0$. Specially in the case

of silicate glasses softening may start more than 100 K lower than the conventional measured $T_{g(qT=10K/min)}$. In many studies that effect has been disregarded when a statement was given that a material was probed below T_g . To avoid relaxation processes from liquid fractions an investigation of glasses should always performed below T_{g_0} or even better below T_{g_g} . An equal disregard frequently appears with investigations of the liquid state, f. e. measurement of viscosity covering as well the regime above $T_{g_{liq}}$ as the range near T_{g_0} .

Conclusions

The most important foundations of the new model - one may call it “size proportional and alignment related translation model (SPART)” - are

- generation of apertures of sufficient size by combinative mode amplification allowing molecular shifts without need of additional activation energy,
- strong influence of orientation of molecular axes and thereupon following variable possibilities to move through neighboring gaps,
- limiting volume V_{g_0} and following thereupon a defined time and history independent material-specific glass temperature T_{g_0} for all substances,
- two- to tripartite viscosity behavior of all liquids
- existence of a material specific intermediate limiting volume V_{gl} for simple non-spherical molecules, below molecular translation possibilities adopt a new quality,
- importance of mode distribution approaching V_{g_0} ,
- a *finite* maximum value for equilibrium viscosity at T_{g_0} ,
- different viscosity behavior below and above the melting point of the crystalline phase
- dependence of molecular transport processes on specific volume and thermal expansion
- and, last but not least, strict distinction between relaxation processes and glass transition.

In the author's opinion, the model presented here provides a consistent microscopic view of the glass transition and molecular processes within liquids.

Prospects

In part II of this work (already published as working paper: DOI 10.13140/RG.2.2.21857.61286 - https://www.researchgate.net/publication/319878166_Microscopic_Model_of_Glass_Transformation_and_Molecular_Translation_in_Liquids_II_Strong_Evidence_for_Power_Law_Volume_Dependence_of_Viscosity_-Revised_and_enhanced_issue) the experimental validation of the new model has been performed by regression analysis with new viscosity equations. The new equations are in no case significantly worse and in the very most cases superior to the well known equations of Vogel-Fulcher-Tamman (VFT), Doolittle, MCT, Bässler-Avramov and to new proposed scaling procedures based on equations containing both volume and temperature first developed by Andrade 1934. The basic viscosity equation can be used up to the critical point and at higher exterior pressures with pressure dependent terms without changing the basic parameters. This will be demonstrated by comparison of regression results with NIST and original measuring data from various material classes.

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