

Modern aspects of the kinetic theory of glass transition

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Contents

1. Introduction	42
2. Experimental observations	43
3. Theoretical methods	47
3.1 Fictive temperature concept; 3.2 Vol'kenshtein–Ptitsyn relaxation theory; 3.3 Free-volume models; 3.4 Tool–Narayanaswamy–Moynihan method; 3.5 Kovacs method; 3.6 Adam–Gibbs theory; 3.7 Configurational entropy approach to glass transition; 3.8 Glass transition in terms of nonequilibrium thermodynamics; 3.9 Some current microscopic approaches to glass transition description	
4. Kinetic criteria of glass transitions	57
4.1 General kinetic criterion of glass transition and examples of its application; 4.2 Width of a glass transition range	
5. Physical relaxation of polymers	60
6. Glass transition kinetics in a wide range of cooling rates	61
7. Conclusions	62
References	64

Abstract. This paper reviews glass transition kinetics models that are developed to describe the formation of structural (for example, covalent and metallic) glasses, as well as to account for the transition of a polymer to a solid glassy state. As the two approaches most frequently used over the last decade to model the glass transition, the Tool–Narayanaswamy–Moynihan model and the Adam–Gibbs theory of glass transition are described together with examples of their applications. Also discussed are entropy-based approaches that rely on irreversible thermodynamics methods originated in the work of De Donder, Mandelstam, and Leontovich. The actual problems that arise in applying these methods and the prospects of their development are discussed. A brief overview of statistical glass transition models is given, including the mode-coupling and energy-landscape theories.

Keywords: glass transition, kinetics of glass transition, polymer glass transition, theory and modeling of glass transition, thermal properties of amorphous solids and glasses

1. Introduction

The glass transition, the dynamical transition of a system from a thermodynamically equilibrium liquid state to a frozen-in thermodynamically nonequilibrium (glassy) state, can be regarded as one of the earliest technologies humans tapped to fabricate materials [1–4]. With new materials being invoked and increasingly higher variation rates of temperature and other external parameters becoming available, new glass fabrication methods are now emerging and their range of application continuously expands. One finds numerous examples of how solid amorphous materials produced in the glass transition are used in every sphere of human activity and industry. One such example is polymers, namely materials which have a wide range of applications and show enormous promise for the future.

The fact that the final state of a material is strongly dependent on its cooling rate and thermal prehistory imparts great applied importance to the problem of the theoretical description of the glass transition process. Considerable optimization can be achieved for glass-based production processes and for the performance of glass-based products with a theory capable to quantitatively account for glass transition in various materials. However, neither the glass structure itself nor the glass formation kinetics have yet been given a sufficient explanation at the microscopic level and thus they represent an intriguing problem for condensed matter physics.

Although low-molecular materials, polymers, metallic glasses, and other glass-forming systems differ considerably in their molecular structure whether in a liquid or a solid amorphous state, there is much observational evidence that,

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when changed to glass, their macroscopic characteristics are essentially similar. For example, the specific volume, thermal expansion coefficient, enthalpy, elastic modulus, and other material properties change in a qualitatively identical manner in completely different materials, irrespective of their molecular structure, suggesting that a general theory should exist that is at least capable of predicting how their macroscopic properties evolve.

The challenge of creating such a general theory is well illustrated by the fact of existing various and diverse phenomenological approaches to and theories for describing the glass transition process that in some cases differ fundamentally in some aspects and which are too numerous to describe in detail within a single review. This diversity itself implies, however, that the theory of glass transition currently represents one of the most significant unsolved topics in theoretical physics. The important point here is that, in addition to the well-known problems of describing real equilibrium systems by statistical physics methods, one faces problems related to the change in and the rate of change of the external parameters involved. Thus, opinions still vary as to whether glass transition is a purely dynamic process which ‘freezes’ relaxation phenomena characteristic of liquids or whether, at least under some conditions, it results from the existence of a special thermodynamic phase, for example, so-called ideal glass. A further point to note is that, as tools for describing experimental data, theoretical methods formulated over fifty years ago still remain popular. However, the last few decades have seen active attempts to develop new microscopic approaches closely relying on the laws of statistical physics and, hence, on the employment of computer simulations capable of implementing various (including *ab initio*) calculation methods.

This review systematically summarizes the approaches that are currently most widely applied for describing the glass transition kinetics. Because, as mentioned, the glass transition process is similar for completely different materials, the theoretical methods are usually described here without regard for the structural features or properties of a specific material. The examples chosen and references cited mainly reflect the author’s research interests, which in recent years have concerned the description of experimental data on polymers. This approach does not lead to a limitation of the range of application of the methods to be described; they are quite successful in describing the glass transition in any material. Furthermore, the methods to be discussed are also of interest for describing glasslike states that arise at phase transitions, such as structural transitions [5, 6] and superconducting transitions occurring in high-temperature superconductor glasses [7–9]. Mention should also be made of similar states observed in disordered crystals [1].

On the other hand, the methods developed in the theory of phase transitions (for example, in the theory of spin glasses) are also utilized in the general theories of glass transition, and similar ideas appear in related fields such as the study of metallic [10], dipole [11], and polymer [12] glasses.

The particular emphasis of this review is on the application of established phenomenological models to the theoretical methods under discussion because, despite their high promise, current microscopic theories cannot yet quantitatively describe the glass transition kinetics of complex systems. Moreover, such phenomenological approaches provide a general picture which, as is the case in classical

thermodynamics, can be developed further through the employment of microscopic methods.

The review outline is as follows. Section 2 briefly presents what is typically observed experimentally in glass transitions. Section 3 supplies step by step a chronological account of the theoretical methods that have been developed for describing glass transition kinetics, starting from Tool’s concept of fictive temperature and ending with the mosaic and mode-coupling theories. Section 4 presents the generalized kinetic glass transition criterion and discusses the general implications of the criterion and its application to the study of the effect of cooling/heating rate on the glass transition temperature and the width of transition interval. Section 5 briefly discusses recent advances in the theoretical description of the physical relaxation of polymers. Section 6 presents the results of modeling of the glass transition of polymers in a wide range of cooling/heating rates and discusses the challenges that exist in this field. The concluding section discusses the results of some studies, examines topical problems in glass formation kinetics, and explores prospects of theoretical approaches to solving these problems.

2. Experimental observations

The way in which a diversity of properties of a system (the specific volume, enthalpy, etc.) evolve in time as a glass transition proceeds can give a clue to the basic features of the process. This is clearly exemplified by the behavior of a certain property p for two temperature ‘histories’ which qualitatively correspond to most experimental situations: (1) a sudden switch of temperature, when it abruptly changes by ΔT throughout the system, and (2) a temperature decrease at a certain (usually constant) rate $q = dT/dt$. For a stepwise isobaric change in temperature, the glass transition region reveals two contributions to the change in p : one of them instantaneous (isostructural), and the other relaxational (structural) (Fig. 1a). The former type of response (which remains relevant for a glassy state as well) reflects how the thermal vibrations of the material’s particles (phonon contribution) change their nature as a result of the change in the external conditions, whereas the latter response mechanism is due to a change in the structural characteristics of the system and remains inoperative in the ‘frozen-in state’ of the material.

An important feature distinguishing glass transition relaxation from relaxation processes in many other systems is that, for structural relaxation, the chosen parameter p varies *nonexponentially* with time t . Whereas relaxation in a liquid at sufficiently high temperatures follows the law $p(t) \sim \exp(-t/\tau)$ (where τ is the characteristic relaxation time), in the glass transition region we observe a strong deviation from this law, with different properties of the system possibly demonstrating different behaviors [13, 14]. The response function in this case is most commonly—and quite reasonably—approximated by the so-called Kohlrausch law, $p(t) \sim \exp[-(t/\tau)^\beta]$ [15, 16], where β is a positive factor less than unity, usually $0.35 < \beta < 0.75$ [2]. The case of β equal to unity corresponds to Maxwell’s exponential relaxation behavior, whereas $\beta < 1$ results in what is known as stretched exponential relaxation. Another feature of this relaxation is its *nonlinear* nature, which manifests itself in the relaxation time τ depending on both the conventional thermodynamic parameters (temperature, pressure, glass composition) and additional structural parameters of the

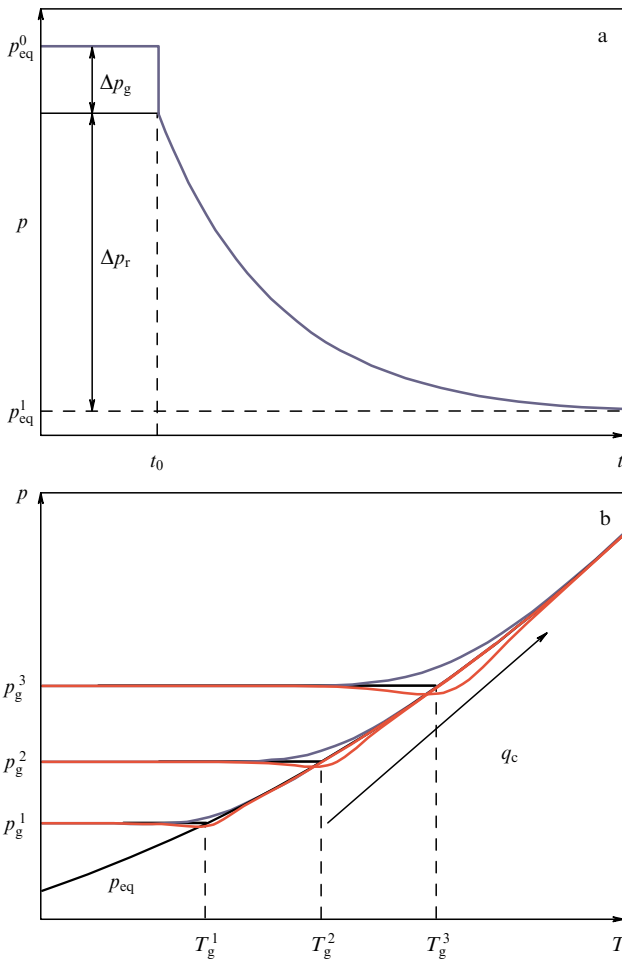


Figure 1. (Color online.) A characteristic response of a glass-forming system expressed in terms of the dependence of p on temperature or time (a) for a jump in temperature, and (b) for a liquid-to-glassy state transition at a constant cooling rate (blue lines) and a subsequent heating (red lines). Here, p_{eq} , p_{eq}^0 , and p_{eq}^1 are the equilibrium values of the property p for different temperatures; q_c is the heating/cooling rate, which assumes three values; T_g^1 , T_g^2 , and T_g^3 are the glass transition temperatures for the respective values of the rate q_c , and p_g^1 , p_g^2 , and p_g^3 are the corresponding values of the property p which are ‘frozen-in’ during the glass transition.

glass that appear in a thermodynamic description due to the departure of the glassy state from equilibrium [1–3].

Figure 1b illustrates how a system’s property p being studied (say, enthalpy, specific volume, etc.) evolves as the system is uniformly cooled at different constant rates from a liquid state [17, 18]. As the temperature decreases, the relaxation time of the system increases, resulting in the deviation of the observed values of p from the equilibrium value p_e in a certain range of temperature T , so that p assumes a certain ‘frozen-in’ value p_g on the time interval of experimental observations. Note that the higher the cooling rate q , the larger the ‘frozen-in’ value p_g . If upon completion of cooling the temperature is steadily increased (a glass-to-liquid transition), then the behavior of p in the glass transition region will differ from its behavior during cooling, giving rise to hysteresis. There is a wealth of experimental evidence that supports this result and which also shows that the glass transition temperature depends on the heating/cooling rate. Other material properties, such as the isobaric heat capacity C_p , vary with temperature in a different way (as the derivative

with respect to T of the dependences depicted in Fig. 1b), showing a monotonic change in the glass transition region from a linear behavior for a liquid to a different linear behavior for a glassy state. At the reverse transition, a nonmonotonic curve with one or two heat capacity peaks is observed if the heating proceeds sufficiently fast (faster than the cooling rate).

One of the key conclusions to draw from the curves plotted in Fig. 1 is that the glass transition is essentially a kinetic process. The evolution of the properties of a system depends on both the rate of change of the external parameters (here, temperature) and the time needed for the system to relax to the corresponding equilibrium state. To describe the kinetic transition to a glassy state, various combinations of these parameters have been proposed, starting from the works by Bartenev, Jones, Ritland, Volkenstein, and Ptit-syn, which have led to the development of a number of criteria (see Refs [14, 19] for a review). As a generalization of the earlier proposed criteria, Refs [14, 19] also formulated a glass transition criterion based entirely on a general thermodynamic analysis of the glass transition, without relying on any specific models of a glass-forming system. This generalized criterion requires that the relaxation time τ_R of the structural parameter of the system be equal to the characteristic time for the variation of the glass transition-inducing external factor. If the transition of the system to a glassy state is due to a change in temperature, then the characteristic time for the variation of temperature τ_T can be written as

$$\tau_T = \left(\frac{1}{T} \left| \frac{dT}{dt} \right| \right)^{-1}. \quad (1)$$

Then, the condition for the transition from an equilibrium liquid state (in which $\tau_R \ll \tau_T$) to a ‘frozen-in’ glassy state ($\tau_R \gg \tau_T$) is as follows: $\tau_R \sim \tau_T$ [14, 19], from which the glass transition temperature T_g can be estimated as

$$\left(\frac{1}{T} \left| \frac{dT}{dt} \right| \tau_R \right) \Big|_{T=T_g} \approx 1. \quad (2)$$

References [14, 19] show that the earlier developed glass transition criteria are limiting cases, or approximations, of general criterion (2). Notice also that if a transition to a glassy state is caused by changes in other external parameters determining the state of the system (for example, pressure), then the generalized criterion remains unchanged in form requiring merely that τ_T is replaced by the characteristic time for the variation of the corresponding parameter (see Section 4.1 for more detail).

Using the glass transition criterion (2) and employing the appropriate expressions for the relaxation time of a specific system, it is possible to obtain analytical expressions for the glass transition temperature as a function of the cooling/heating rate. This was first done by Bartenev [20], who approximated criterion (2) as $q|\tau_R| \approx \text{const}$, where $|q|$ is the heating (or cooling) rate of the system. Assuming the temperature dependence of the relaxation time to be defined by $\tau_R = \tau_{R0} \exp[-A/(k_B T)]$, Bartenev obtained the expression, now known as the Bartenev–Ritland equation [20–22], for the dependence of the glass transition temperature on the rate q :

$$\frac{1}{T_g} = C_1 - C_2 \ln q, \quad (3)$$

where the material parameters C_1 and C_2 are determined from the relaxation behavior parameters. Using general criterion (2), it can be shown that C_1 is not a constant, but rather a function weakly dependent on T_g [which does not usually greatly affect dependence (3)].

There is abundant experimental evidence that the dependence of the glass transition temperature T_g on the heating/cooling rate is usually described well by formula (3) over a wide rate range. The reason is that, for this quite wide but still limited temperature range, the relaxation time is well described by Maxwell's expression Bartenev used. However, for a wider range of the temperature variation rate, the glass transition temperature T_g varies over a wider range, making it necessary to derive a more accurate expression for the relaxation time [hence, deviations from equation (3)].

The dependence of the structural relaxation time on temperature is reflected in the temperature dependence of the viscosity of a supercooled liquid. It is a long-known fact that the properties of glass-forming systems have qualitatively different temperature dependences. Indeed, glasses are known to be technologically divided into 'short' and 'long' types depending on how fast the viscosity in the region of the glass transition changes with temperature (see, for example, Ref. [1]). To describe these differences in the behavior of glass-forming melts by dependences of the form $\eta(T)$ or $\tau(T)$, Angell [23] rather recently proposed a new parameter, the fragility index, with which to quantify the deviation from the Arrhenius behavior. Materials that exhibit a typical Arrhenius behavior of $\eta(T)$ are classified as strong, and those deviating mostly from it as fragile. For the latter, the viscosity increases sharply in the glass transition region.

Notice, however, that Angell's classification and its consequences only make sense when the glass transition temperature is defined for all liquids in the same way, from the viscosity value of 10^{12} Pa s independent of the heating or cooling conditions (rates), in accord with Tammann's [24] suggestion about the definition of T_g (see Ref. [25] for details). However, as can be seen already from the Bartenev–Ritland equation (3), temperature—and hence viscosity—can, depending on the cooling or heating rate, assume very different values at the glass transition. Therefore, any criterion specifying the value of viscosity at T_g is of limited value as a tool for stimulating the understanding of glasses and glass transitions.

Whatever theoretical arguments and discussions there are on the value of the fragility index for describing the glass transition, experimental studies show that the temperature dependence of the viscosity of supercooled glass-forming liquids generally tends to be well described by the phenomenological Vogel–Fulcher–Tammann (VFT) equation [26–28]

$$\eta(T) = \eta_0 \exp\left(\frac{B}{T - T_0}\right), \quad (4)$$

where η_0 , B , and T_0 are material-specific constants. Therefore, the glass transition is appropriately described by applying Eqn (4) as an expression for the characteristic relaxation times with a corresponding factor for the passage from $\eta(T)$ to $\tau(T)$. It can be shown [1, 17, 18] that over a wide range of q rates, the Bartenev–Ritland law is satisfied for strong glass-forming systems, and takes a different form for fragile ones (see Section 4).

Equation (4) adequately describes the behavior of the so-called equilibrium viscosity of a liquid, which leads to a similar behavior for the equilibrium relaxation time. As mentioned above in connection with Fig. 1, one more important feature of glass transition is the so-called memory of the material. In this effect, both the thermodynamic and kinetic characteristics of the system, including the way it relaxes to equilibrium, depend not only on the current values of properties of the system (such as pressure, temperature, and the molar fractions of the components) but also on its previous thermal history. The memory effect was observed in early experiments for the example of the refraction index of glasses hardened in different ways; for other experiments revealing these effects, see Refs [29–33].

Hence, not only do the usual thermodynamic parameters such as temperature, pressure, and molar fractions have to be taken into account in describing the evolution of the material's properties in the glass transition process, but so does the thermal history of the material. The inclusion of the memory effect is of interest from a theoretical point of view because it turns out to be not sufficient to consider a first-order differential equation for a single order parameter for a proper description of the glass transition. In order to develop an appropriate theoretical description, different approaches to the problem may be applied: one can either to consider relaxation of several structural parameters by setting up a system of coupled first-order differential equations, or, on the contrary, to develop a theory with a single structural order parameter introducing, in doing so, 'memory' integrals over the thermal history of the process.

There is a wide range of methods for experimental investigations of glass transitions and glass properties. One of the most effective current methods of experimentally exploring the glass transition in various materials is differential scanning calorimetry (DSC). With the development of new experimental techniques, the previously accessible DSC cooling rates of at most a few kelvins per second increased by many orders of magnitude up to 10^6 K s⁻¹ [34–37], thus reaching the lowest limits accessible to computer simulation. Having regard to the way they are used and given the extremely long duration of the experiment (for example, cooling to 100 K takes about three years at 10^{-6} K s⁻¹, and three months at 10^{-5} K s⁻¹), the unique possibility arises of investigating the glass transition over the cooling rate range of more than ten orders of magnitude. An alternative (or supplementary) approach constitutes temperature-modulated calorimetry (TMC) [38–41] for the study of the phenomenon of dynamic glass transition (or TMDSC if different device realizations are employed). An experimental study in this case consists of exposing a system to small-amplitude temperature oscillations at a given frequency ($\delta T(t) \sim \exp(i\omega t)$) and then analyzing the system's response. The experimentally accessible frequency range extends from a few μ Hz to a few hundred kHz for laser alternating current (AC) calorimetry. It should be noted that measurements in this range of ω and q require the employment of several experimental techniques (and, hence, of various devices), as well as the use of samples widely differing in volume (mass) (see, for example, Refs [42, 43]).

Temperature oscillations in the present-day devices are usually accompanied by the cooling or heating of the sample at a preassigned constant rate. In some cases, two glass transition temperatures may be recognized, one of which corresponds to the transition described above, and the other,

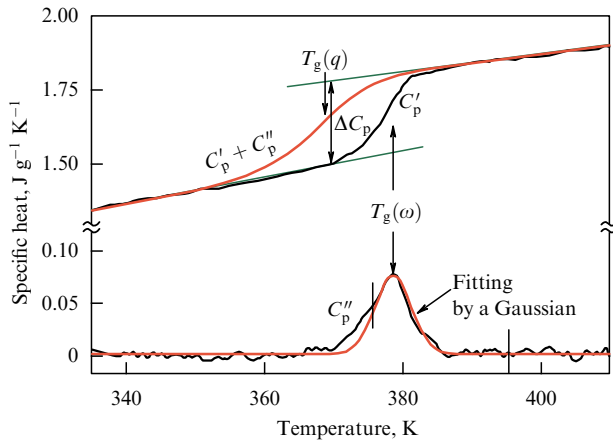


Figure 2. Temperature dependence of the specific heat capacity of polystyrene as measured by TMDSC [44].

the dynamic one, to the retardation in the relaxation to equilibrium of some ‘internal’ system’s modes with respect to fast temperature oscillations [44, 45]. The former glass transition temperature depends on the cooling rate, $T_g(q)$, and the second on the temperature oscillation frequency, $T_g(\omega)$. Figure 2 presents the results of such measurements on polystyrene. References [46–48] obtained expressions relating q and ω for the observed transitions, and Refs [42, 49, 50] showed good agreement with experimental data over a wide frequency range for different samples. The reader is referred to handbook [51] for a review including a description of the basics of TMDSC technique and its application to polymer studies.

The schematic model of the dynamic glass transition is similar to Herzfeld’s and Rice’s model of sound absorption in polyatomic gases [52], which introduces a relaxation time accounting for energy transfer from the system’s internal to external degrees of freedom. In this case, one can introduce a complex-valued dielectric constant, with its real and imaginary parts determined experimentally. Similarly, for a model with a constant energy transfer relaxation time, the frequency dependence of C_p is found to be given by [53–55]

$$C_p^*(\omega) = C_p' - iC_p'' = C_{p,\infty} + \frac{C_p^i}{1 + \omega^2\tau^2} - i \frac{C_p^i\omega\tau}{1 + \omega^2\tau^2}. \quad (5)$$

From Eqn (5) it is seen that at a certain value of temperature oscillation frequency ω the imaginary part of $C_p(\omega)$ reaches a maximum, and just this value is associated with the dynamic glass transition. Situations that occur in real systems are more complex and require including a distribution of relaxation times and considering how this distribution varies with temperature.

Much of the experimental and theoretical work has been focused on the structural relaxation (‘aging’) of a material held at temperatures $T_a < T_g$ [56–60], where T_a is located within the glass transition range. This holding is followed by further cooling to a preassigned temperature beyond the glass transition range. For a number of polymers, such as polystyrene, polymethacrylate (PMA), and polymethyl methacrylate (PMMA), measured data are available for both short-time relaxation (from 0.01 s) and annealing for one year and longer [58, 61–65]. The results are presented in the form of the time dependence of the enthalpy regained by the system during its annealing (as opposed to that for a sample cooled without annealing).

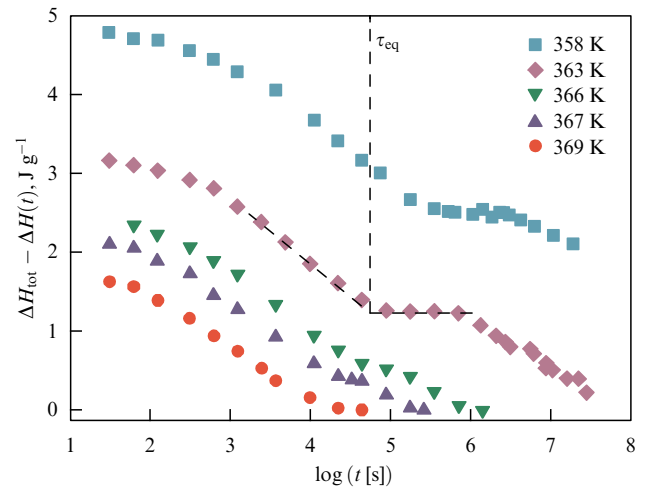


Figure 3. DSC observations of two-stage relaxation in polystyrene [65]. $\Delta H(t)$ is the restored enthalpy at instant of time t , and $\Delta H_{tot}(t)$ is the total enthalpy which the system can restore. Annealing temperatures are shown.

Over the last decade, a discussion in the literature has been aroused as to whether a system, if given enough time, reaches a state with an enthalpy extrapolated from the data for the liquid, i.e., extrapolated to the equilibrium value, or whether, as some theorists have hypothesized, a new metastable limit exists for $T < T_g$ [66]. One fundamentally important recent finding in this area — specifically, in the study of structural relaxation in polystyrene and polycarbonate — is an observation of two-stage relaxation mechanism [63, 65]. From the experimental data shown in Fig. 3, it is seen that the initial relaxation at sufficiently low temperatures T_a is followed by a time plateau, which can be of various durations and which is, in turn, followed by a renewed structural relaxation ultimately bringing the system to equilibrium. These results continue to be discussed, and new experimental data are expected to come very soon.

From the perspective of investigating the behavior of the properties of various systems in the glassy state, it is also of interest to study variations in these properties and the glass transition kinetics under conditions of confining system’s dimensions [10, 67]. Such studies are primarily concerned with the glass transition in pores or film-shaped materials [34, 68–71]. There is considerable recent interest in polymer thin films due to the fact that their thickness can be varied virtually continuously from a few micrometers to a few nanometers [68]. One aspect of this interest is the current miniaturization trend in industry (in particular, in microelectronics).

There is a variety of techniques for determining the glass transition temperature of a film, including ellipsometry, dilatometry, X-ray diffractometry, dielectric spectroscopy, and DSC. For substrate-supported polymer thin films, it has been shown by various methods that, as the film thickness is decreased to below 300 Å, the glass transition temperature decreases to within 25 K of the initial, ‘bulk’ value T_g [72]. A similar effect has been observed in thin films of other polymers [73, 74]. Studies of PMMA revealed the influence of the substrate type (and, hence, of the polymer–substrate interaction) on the dependence of T_g on the film thickness d [75, 76]. It is found that the effect depends on the chain length (molar mass) of the polymer: linearly for heavy and non-linearly for light polymers (in the latter case, the dependence is identical to that for a substrate-supported film [77]).

Over the last decade, it has become clear from simultaneous measurements of the molecular dynamics and glass transition temperature of thin polymer films that the reduction in T_g with decreasing d has no direct relation to the change in the relaxation time of the polymer [71, 78–80]. It is conjectured that just the geometry on the nanoscale (for example, the film thickness) markedly influences the relaxation time of the sample studied (which affects the obtained values of T_g), whereas the relaxation time determined by molecular dynamics again corresponds to the bulk values [69].

The standard properties and kinetic parameters of glass-forming materials are currently measured routinely both for polymers and other materials. As a result, the totality of accumulated data is so vast that already years ago many electronic databases, some structured by system types and some by property types, were developed [81–83]. Mention should also be made of a number of excellent reviews concerned with the glass transition [23, 84–95], in which the observed behavior patterns and theoretical approaches are discussed.

Overall, the experimental observations described in this section adequately reflect the nature of the kinetics of the glass transition considered as a kinetic phenomenon, which makes it possible to proceed to discussing the theoretical foundations of the process.

3. Theoretical methods

The phenomenological description of the kinetics of the glass transition has a history of over 80 years [1–4, 96]. A simplified view of the glass transition as a transition from an equilibrium liquid to a ‘frozen-in’ state of glass proceeding at a discrete value of temperature T_g was proposed by Simon [97, 98]. In such a treatment, it is conjectured that for $T > T_g$ the system can achieve equilibrium at a rate greatly exceeding the rate of changing the external parameters, whereas for $T < T_g$ the system finds itself in a frozen-in nonequilibrium glassy state and, according to experimental observations, is unable to reach the equilibrium state. There exists, however, conclusive experimental evidence that glass transitions actually occur in a certain temperature range $T_g^- < T < T_g^+$. These experimental data are consistent with Tammann’s [24] description of the glass transition expressed nearly at the same time as Simon developed his ideas. As shown below, the width of the glass transition region increases with increasing the rate of changing temperature. Sections 3.1–3.9 present and discuss the basic features of currently employed methods of description of the glass transition kinetics.

3.1 Fictive temperature concept

The concept of structural (or, alternatively, fictive) temperature T_f was introduced by Tool as an additional characterization parameter for the purpose of describing the supercooled liquid–glass transition of a system [99–101]. It is, by definition, the temperature at which “a given system will be in the equilibrium state if heated at a sufficient rate” [100]. Thus, it is assumed that in this state the system has the same structure as the glass under study, but at a temperature T_f it is in equilibrium. The rate of the system relaxation to equilibrium in this case is determined by the difference between the system’s current temperature T and its fictive temperature T_f , and also by the kinetic factor which is inversely proportional to viscosity. In Ref. [100], a qualitative (but not quantitative) correspondence is reported to exist between the experimental

and model curves for the evolution of some properties of the system, utilizing these concepts.

The concept of fictive temperature is still actively used even today in the analysis of experimental data in some model frameworks. Thus, from DSC data it is possible to determine the limiting fictive temperature T_f' (corresponding to the ‘frozen-in’ value of T_f) as an integral characteristic of the C_p curve [102]:

$$\int_{T^*}^{T_f'} (C_p^{\text{liq}} - C_p^{\text{gl}}) dT_f = \int_{T^*}^{T'} (C_p - C_p^{\text{gl}}) dT, \quad (6)$$

where T^* is a certain temperature beyond the glass transition region at which the heat capacity is equal to its equilibrium value $C_p^{\text{liq}}(T)$; T' is a temperature well below the glass transition region, $T' \ll T_g$, and $C_p^{\text{gl}}(T)$ is the extrapolated linear dependence of the glassy state heat capacity. Currently, this definition of T_f' tends to be viewed as referring to the glass transition temperature T_g as measured by DSC [88, 103]. According to models that rely on the relaxation of enthalpy, the evolution of the fictive temperature is directly related to the heat capacity by

$$C_p^{\text{red}} = \frac{dT_f}{dT}, \quad (7)$$

where C_p^{red} is the reduced isobaric heat capacity given by

$$C_p^{\text{red}}(T) = \frac{C_p(T) - C_p^{\text{gl}}(T)}{C_p^{\text{liq}}(T) - C_p^{\text{gl}}(T)}. \quad (8)$$

It is seen that, with this definition, the heat capacity equals unity for $T \gg T_g$, and zero for $T \ll T_g$. It should be noted that totally different definitions of the structure parameters are possible (see, for example, the earlier work [104] or discussion in Ref. [105], and criticism of the T_f approach in Ref. [106]), but the fictive temperature concept has proved to be a suitable framework for the quantitative description of the glass transition. While the simplified model initially advanced by Tool is no longer utilized to describe experimental data, some of the more sophisticated models still in use and considered in Sections 3.2–3.9 employ it as their basis.

3.2 Vol’kenshtein–Ptitsyn relaxation theory

The theory of the glass transition developed by Vol’kenshtein and Ptitsyn [107, 108] based on the analysis of transitions in the framework of a two-state model provides a means to qualitatively describe both the kinetics of the glass transition process and the general dependence of its features on the heating and cooling rates of the system.

This theory considers the transitions of the kinetic elements of the system between states 1 and 2 with probabilities of ω_{12} and ω_{21} ; the molar fractions of these elements in these states satisfy the equality $v_1 + v_2 = 1$. Then, for v_2 we have the following equation

$$\frac{dv_2}{dt} = -\frac{1}{\tau} (v_2 - v_2^{\text{eq}}), \quad (9)$$

where v_2^{eq} is the equilibrium value of v_2 , for which $dv_2/dt = 0$, and τ is the relaxation time of the system. Both these values are determined by the transition probabilities which, in turn, depend on the temperature and pressure of the system:

$$\tau = \frac{1}{\omega_{12} + \omega_{21}}, \quad v_2^{\text{eq}} = \frac{\omega_{12}}{\omega_{12} + \omega_{21}}. \quad (10)$$

In their examination of the general form of the solution to equation (9) for heating and cooling processes occurring at a constant pressure and for T -dependence of v_2^{eq} assumed to be weaker compared to the relaxation time, the authors of Ref. [100] conducted a detailed analysis of how the quantities linear in v_2 and the derivatives dv_2/dt corresponding to the heat capacity vary with temperature. The variations obtained are in qualitative agreement with experimental data in terms of the heat capacity peak and v_2 hysteresis for various heating-to-cooling rate ratios.

Vol'kenshtein and Ptitsyn also arrived at an estimate for the dependence of the glass transition (softening) temperature on the cooling (heating) rate [107]:

$$\left. \frac{d\tau}{dT} \right|_{T_g} \sim -\frac{1}{q(T_g)}. \quad (11)$$

Expression (11) provided a correct description (at least qualitatively) of the then available experimental data on the glass transitions in liquids and polymers (see, for example, Refs [20, 21, 109]). Meanwhile, such a model, with τ considered as a function of temperature (pressure) alone, fails to account for some fundamental properties of the glass transition process, one example being the memory effect. Despite their simplicity, the key aspects of Vol'kenshtein's and Ptitsyn's theory are used, variously modified, even in its simplest version in current approaches to the description of glass transition. A few years later, Cooper's and Gupta's numerical calculations [110] independently led them to a formulation of a criterion analogous to Eqn (11). As shown in Refs [14, 19], expression (11) can be derived as a direct consequence of general criterion (1) by taking the derivative with respect to temperature. If, in addition, τ is considered a function not only of pressure and temperature but also of the corresponding structural order parameters of the system [14, 19], then the memory effect may also be introduced into the model. Note, however, that in our opinion it is expression (1) which is the primary glass transition criterion, and expressions like (11) are merely some of its particular consequences.

3.3 Free-volume models

Underlying the phenomenological free-volume models are the basic hypotheses advanced in Refs [111–114] (see Ref. [3] for the details and description of the early work in this area). The models assume, as is natural, that a certain additional space, a 'free' volume, is always required for the molecular structure to be rearranged. Because the volume occupied by a fluid decreases with cooling, the volume accessible to the molecules decreases, reducing the occurrence probability of the rearrangement necessary for the transition to an equilibrium structure.

Denoting the free volume per molecule by v_f , the model predicts that the relaxation time can be described via [112]

$$\tau = \tau_0 \exp\left(\frac{C}{v_f}\right), \quad (12)$$

where the constant C is material-specific.

The key question in this case is how to define what the free volume accessible to a single molecule in the fluid is. The definitions vary depending on the approaches used. Initially [111], the free volume was defined as the difference between the current volume and the volume the system will occupy after a hypothetical extrapolation to zero temperature; hence,

$v_f \rightarrow 0$ as $T \rightarrow 0$. In another definition, v_f is that part of the volume of the fluid which can be rearranged without energy loss. According to Refs [112, 115], $v_f \rightarrow 0$ is realized already at a finite temperature, and the relaxation time is given by an expression similar to Eqn (4).

Treating viscosity as simultaneously dependent on the free volume and (directly) on the temperature is discussed in Refs [61, 116–118]. For example, Ref. [116] modifies the initial expression (12) to take into account the activation nature of particle hopping from accessible pockets:

$$\tau = \tau_0 \exp\left(\frac{A}{RT} + \frac{C}{v_f}\right) = \tau_0 \exp\left(\frac{A}{RT} + \frac{B}{T - T_\infty}\right), \quad (13)$$

where R is the molar gas constant, while A and B are material parameters.

Currently, the free-volume model is rarely applied for modeling purposes because it is now a well-established fact that the relaxation time is not a function of the fluid density alone. Of present-day relevance, though, is the application of its elements to describe the existing data on the structural relaxation of polymers. Thus, Ref. [119] considers modifications of the Adam–Gibbs theory, which are based on the free volume approach, and suggests two expressions for the relaxation time τ , which are used in describing experimental DSC data on polystyrene: the glass transition upon cooling at a rate of 0.1–100 K s⁻¹, and structural relaxation upon holding at 363 K for no longer than 20 h. Compared to the VFT expression, a more accurate fit to the experimental data is achieved.

3.4 Tool–Narayanaswamy–Moynihan method

The Tool–Narayanaswamy–Moynihan (TNM) method based on Tool's concept of fictive temperature and Narayanaswamy's seminal 1971 paper [120] is widely applied even today to analyzing experimental data. Following the publication of Narayanaswamy's paper, Moynihan and colleagues proposed algorithms for calculating the properties of glass under the conditions of isothermal relaxation and temperature being varied at a fixed rate [121, 122] (hence, TNM).

In Ref. [120], the response function of the property p to an instantaneous isobaric temperature change is expressed in the form

$$M_p(t, \Delta T) = \frac{p - p_{2,\infty}}{p_{2,0} - p_{2,\infty}} = \frac{T_{fp} - T_2}{T_2 - T_1}, \quad (14)$$

where the subscripts 0 and ∞ denote, respectively, the instantaneous and infinite-time values of p ; the response function is unity at initial time and zero at infinite time. The nonlinearity of relaxation is reflected in the dependence of M_p on ΔT . The quantity T_{fp} in Eqn (14) is the so-called fictive temperature corresponding to the property p (i.e., different fictive temperatures can be introduced for various properties). The equilibrium response function is defined by the limit of $\Delta T \rightarrow 0$, subject to the departure from equilibrium.

In Ref. [123], Narayanaswamy makes the following three assumptions in his mathematical glass transition kinetics model which necessarily accounts for nonlinearity, nonexponentiality, and memory effects featuring a given process. First, structural relaxation is considered as a single, non-exponential, constant-activation-energy mechanism. Second, the form of the equilibrium response function does not depend on the current value of the system's temperature or

on its fictive temperature (an assumption extending the principle of thermorheological simplicity). And third, the driving force and response are related linearly, leaving the dependence of the relaxation time (or viscosity, according to Narayanaswamy) on the structural parameter of the system as the only source of the nonlinearity of the glass transition.

From these three assumptions, one can deduce a linear response function to a finite temperature (T) or structure temperature change. This can be achieved by introducing a reduced time scale ξ :

$$\xi = \int_0^t \varphi(T, T_{fp}) dt', \quad (15)$$

where the function φ describes the time shift of relaxation (or viscosity) according to the empirical formula

$$\ln \varphi(T, T_{fp}) = \ln \frac{\eta}{\eta_B} = \frac{H_g}{R} \left(\frac{1}{T_B} - \frac{1}{T} \right) + \frac{H_s}{R} \left(\frac{1}{T_B} - \frac{1}{T_{fp}} \right), \quad (16)$$

where T_B is a certain reference temperature for the definition of viscosity η_B , while H_g and H_s are constants equivalent to the activation energies of instantaneous and structural changes, respectively. Using Eqns (15) and (16) and applying the superposition principle (as allowed by the linearity of the response function), the time evolution of the property p being considered is given by

$$p(t) - p(0) = p(0)\alpha_{pl}(T - T_0) - p(0)\alpha_{pe} \int_0^\xi M_p(\xi - \xi') \frac{dT}{d\xi'} d\xi', \quad (17)$$

where α_{pl} is the change rate of the property p , $\alpha_{pl} \sim (dp/dT)_1$, and α_{pe} is the contribution to α_{pl} owing to the structural relaxation of the system.

In equation (17), the change in p is presented as the difference between its value after complete relaxation and that part of the relaxation which is not achieved over the time passed. The author of Ref. [120] took M_p to be the sum of two or more empirically parameterized exponentials to describe the relaxation of the refractive index in some glasses. The evolution of the heat capacity of the material at the glass transition is described by taking the parameter p to be the enthalpy of the system and usually by assuming that its relaxation time is given by an expression identical to that for the temperature dependence of the viscosity. Currently, the relaxation time is usually written in the modified form [121]

$$\tau(T, T_f) = \exp \left[\ln \tau_0 + \frac{\Delta h^*}{RT} x + \frac{\Delta h^*}{RT_f} (1 - x) \right], \quad (18)$$

where the parameter x is responsible for the nonlinearity of the glass transition, and Δh^* is the material parameter corresponding to the activation enthalpy of the relaxation process.

Narayanaswamy's model [120] was used both by its author [123–127] and by other workers [121, 122]. Moynihan in Refs [122, 128] suggested using Kohlrausch's law as a response function and presented formulas for numerically calculating the evolution of the fictive temperature, irrespective of the temperature history of the system, $T(t)$. For this purpose, the function $T(t)$ is represented as a succession of sufficiently small temperature jumps ΔT_i , which are

followed by a pause of duration Δt_i . Then, the fictive temperature at each calculation step is determined by the following formula:

$$T_{i,n} = T_0 + \sum_{i=1}^n \Delta T_i \left\{ 1 - \exp \left[- \left(\sum_{j=i}^n \frac{\Delta t_j}{\tau_{\text{TNM},j}} \right)^\beta \right] \right\}, \quad (19)$$

where $\tau_{\text{TNM},j} = \tau_{\text{TNM}}(T_j, T_{i,j})$.

A series of TNM studies by Hodge and colleagues [57, 58, 129] reported results on the application of the model to DSC experiments on (primarily) polymers, with the thermal history presented either as the aging (quenching) of the sample at a fixed temperature for different time intervals or as uniform cooling at various rates. This work clearly demonstrated the weakness of the model in that a single set of parameters fails to provide a sufficient fit to a set of experimental heat capacity curves. Also, a detailed study of correlations between the model parameters (in particular, x and β) was made, and it was shown, among other things, that in choosing a minimization procedure with respect to a set of parameters, the interrelations between some of the parameters (for example, Δh and x) should be taken into account. Reference [58] also shows correlations between all parameters of the model for five different polymers and two inorganic glasses, which is interpreted as supporting the cooperative nature of the glass transition.

The TNM method described in Ref. [128] can be regarded as a modern formulation of the approach being discussed. The relaxation time τ in expression (19) may be in any form best suitable for the system under study. The proposed method was tested on systems with different sets of properties and for various materials [102, 120, 129] immediately following its proposal.

The TNM method was also applied to model the dynamic glass transition in various systems. References [130–133] considered temperature-modulated calorimetry model experiments on glycerin, polystyrene, polyvinyl acetate, and some mixed systems using the temperature history of the form $T(t) = T_0 + A \cos(\omega t)$ (in early TMC work) or $T(t) = T_0 - qt + A \sin(\omega t)$ (present day TMDSC), respectively, for temperature oscillations around a fixed value T_0 or for linear heating accompanied by temperature oscillations. At sufficiently high temperatures T , the fictive temperature T_f has the same profile, but as the average temperature of the system is lowered, the oscillations show a delay in phase and become smaller in amplitude. As a result, the system ceases to respond to ambient temperature oscillations. Characteristically, at sufficiently high frequencies ω this occurs at temperatures T_0 exceeding the glass transition temperature for a given cooling rate. The TNM simulation of these phenomena yields a sufficiently accurate description of some experimental results [130, 131] and makes it possible to consider the analytical frequency dependences of the oscillation amplitude and the deviations in the oscillation phase of polymer characterization parameters [132].

TNM method remains even today one of the most widely used tools for processing experimental data. It should be noted that a similar glass property calculation method was simultaneously developed at the I V Grebenshchikov Institute of Silicate Chemistry of the Russian Academy of Sciences [85, 134, 135]. The reader is referred to the excellent book by O V Mazurin [2] for obtaining further insight into the features of this method and for descriptions of Narayanaswamy's method and the similar Kovacs method [117, 136].

3.5 Kovacs method

The method developed in Refs [136, 137] by Kovacs, Aklonis, Hutchinson, and Ramos and known by the abbreviation KAHR can be regarded as an alternative to TNM. Unlike Narayanaswamy's theory, which considers relaxation of only one structural parameter, the fictive temperature T_f , the KAHR model is multiparametric. As its authors argue, this approach is most adequate for describing the glass transition-related memory effect. It should be noted that the four authors also considered simple single-structural-parameter models [117] before they came up with the KAHR model.

There are three basic principles which lie at the heart of the theoretical KAHR method. First, the thermodynamic description of the state of a system is based on the use of order parameters, so different relaxation mechanisms are considered, which operate to bring the system to equilibrium and which are described by a distribution of relaxation times τ_i . This spectrum is assumed to be invariant, meaning that temperature and structural changes do nothing more than shift it along the logarithmic time scale without changing its shape (i.e., similarly to the TNM method, a thermorheologically simple system is considered) [136]. Second, τ_i is allowed to depend both on the temperature and on the instantaneous state (structure) of the glass, yielding the response nonlinear and asymmetric with respect to the degree and sign of departure from equilibrium. And third, the response function is linearized by modifying the time scale in a certain way, i.e., by introducing a new system's time scale determined by the intensity of spontaneous fluctuations in the corresponding equilibrium state.

Thus, the state of a system is determined by a set of parameters (T, P, ζ_i) , $1 \leq i \leq N$ (here, P is pressure), with $\zeta = \zeta_i(T, P)$ in the equilibrium state. The system's extensive property v (volume, enthalpy) has a total differential of the form

$$dv = \frac{dv}{dT} \Big|_{P, \zeta_1, \dots, \zeta_N} dT + \frac{dv}{dP} \Big|_{T, \zeta_1, \dots, \zeta_N} dP + \frac{dv}{d\zeta_1} \Big|_{T, P, \zeta_2, \dots, \zeta_N} d\zeta_1 + \frac{dv}{d\zeta_N} \Big|_{T, P, \zeta_1, \dots, \zeta_{N-1}} d\zeta_N. \quad (20)$$

In a similar way, we consider the differential for a given property of the system in equilibrium, v_∞ , subtract the expressions, and introduce a relative departure from equilibrium $\delta = (v - v_\infty)/v_\infty$. The quantity δ can, as conjectured in Ref. [136], be decomposed into separate contributions corresponding to the structural parameters of the system:

$$\sum_{i=1}^N \delta_i = \delta, \quad \sum_{i=1}^N d\delta_i = d\delta, \quad \left(\frac{\partial \delta}{\partial \zeta_i} \right)_{T, \zeta_i} = \left(\frac{\partial \delta_i}{\partial \zeta_i} \right)_{T, \zeta_i}.$$

As a result, the initial equation breaks down after some additional transforms into a system of N kinetic equations for separate departures δ_i . For example, the enthalpy of the system can be written as

$$\frac{d\delta_i}{dt} = \Delta C_p q(t) + \frac{\delta_i}{\tau_i}, \quad \delta = \frac{H - H_\infty}{H_\infty}, \quad (21)$$

where ΔC_p is the heat capacity difference between the glass and the fluid, $q(t)$ is the time dependence of the heating/cooling rate of the system, H and H_∞ are, respectively, the system's current and equilibrium enthalpies, and τ_i is the

relaxation time spectrum of the system. In Ref. [136], analogous to the TNM method, the response to a jumpwise or linear or arbitrary change in temperature was studied, and the realization of the memory effect in the framework of the method was demonstrated. The behavior of the model $C_p(T)$ curves as functions of experimental parameters and the nonlinearity parameter was given a detailed analysis in Ref. [138].

The initial formulation of the KAHR method [136] assumed that each parameter τ_i depends not on the individual deviations δ_i (or a set $\{\delta_i\}$) but only on the integrated deviation δ :

$$\tau_i = \tau_i(T, \delta). \quad (22)$$

Considering the differences between uniform and non-uniform models of the structural relaxation of glasses, the authors of Refs [139–141] discuss, in particular, the applicability of formula (22) to describing relaxation in systems at high degrees of departure from equilibrium. It is shown that, in the framework of assumption (22), the KAHR model is fully equivalent to TNM in terms of the results produced and predictions [141]. The strongly nonlinear kinetics of enthalpy relaxation should expectedly be described by generalizing the dependence in formula (22), i.e., by replacing there the integrated deviation δ by a set of individual deviations $\{\delta_i\}$. An example of applying the Kovacs method to the glass transition in thin films is given in Ref. [142].

References [143] and [144] carried out KAHR simulations of the dynamic glass transition for, respectively, a system with a single relaxation time and a distribution of τ_i 's; demonstrated the efficiency of the method for describing TMDSC data, and examined the dependence of the components of the complex dielectric constant on the cooling/heating rate, the amplitude and period of temperature oscillations, and on the parameters of nonexponentiality (β) and nonlinearity (x).

3.6 Adam–Gibbs theory

An expression relating the relaxation time to the entropy of the system was obtained in theoretical work by Adam, Gibbs, and DiMarzio [145, 146]. The authors of Ref. [146] presented a statistical theory for the amorphous state of linear molecular chains and, based on their proposed expression for the partition function of a model chain, obtained formulas for the thermodynamic properties of a model polymer. It was shown that, as the temperature is decreased to a certain value T_2 , the model predicts a second-order phase transition to a state characterized by the uniquely accessible chain configuration. While this state is not accessible experimentally, other states (for $T > T_2$, with a larger set of accessible configurations) correspond to glass. Under these assumptions, expressions for the glass transition temperature and for its dependence on the molecular weight, composition, and other properties of the polymer were obtained. Reference [146] later came under criticism: it was noted that the model concept of a chain of molecules relies on some poorly grounded admissions [147], and that there are doubts as to whether the glass transition, a phenomenon common both to polymers and low-molecular fluids, can be explained in terms of the properties of linear chains. Reference [145] subsequently considered extending these ideas (irrespective of polymer structural features) and derived an expression for the relaxation time of the system, which later made it one of the most cited papers in the field.

A transition to an ‘ideal’ glass state is characterized, as implied by Ref. [146], by the vanishing of the configurational entropy at temperature T_2 . It can, therefore, be assumed that the retarded relaxation of the system in the glass transition region is due to a decrease in the system’s configurational entropy (i.e., in the number of accessible polymer configurations) as the transition temperature is approached. The theory is based on the idea of cooperatively rearranging regions of the material, which implies that the system is divided into subsystems weakly interacting with the macroscopic environment. But then it can be considered that over a sufficiently long period of time the system behaves as an ensemble of N independent equivalent subsystems, each consisting of z molecules. These subsystems are divided into two classes depending on whether cooperative rearrangement is allowed or not. The probability of rearrangement scales as $\sim \exp[-z\Delta\mu/(k_B T)]$, where $\Delta\mu$ is the energy barrier to the rearrangement process (for a single molecule). Clearly, the parameter z equals unity at sufficiently high temperatures, and should approach the entire size of the system as the transition temperature T_2 is approached. The relaxation time τ of the system is inversely proportional to the mean probability of the subsystem rearrangement:

$$\tau = \tau_0 \exp\left(\frac{\Delta\mu S_c^*}{k_B T S_c}\right), \quad (23)$$

where S_c^* is the configurational entropy of the smallest rearrangeable ensemble of particles, and the configurational entropy of the system, S_c , can be estimated experimentally as

$$S_c(T) = \int_{T_2}^T \frac{\Delta C_p(T)}{T} dT, \quad (24)$$

where $\Delta C_p(T) = C_p^{\text{liq}}(T) - C_p^{\text{gl}}(T)$. The shape of the temperature dependence of ΔC_p determines the expression for the relaxation time; it can be shown, for example, that the hyperbolic behavior of $\Delta C_p(T)$ results in formula (3).

Scherer [148] proposed including the nonlinearity of the glass transition in the sense that the configurational entropy should be dependent on the structure of the system as determined by the fictive temperature at the current instant of time t (rather than by T):

$$S_c(T_f) = \int_{T_2}^{T_f} \frac{\Delta C_p(T)}{T} dT. \quad (25)$$

Expressions that follow from the Adam–Gibbs (AG) model can be applied in the TNM framework, i.e., the evolution of the fictive temperature can be traced by substituting various expressions for τ into formula (19). Some authors [148] note that the theoretically grounded AG expression for τ is advantageous over Narayanaswamy’s phenomenological expression. Example applications of the method to enthalpy relaxation in polymers are given in Refs [148–152]. Expressions (23) and (24) can also be used with the Kovacs method [117]. Also of note is the fact that the AG model serves as the basis for a number of modern theories, as exemplified by the often-used hypothesis of cooperatively rearranging regions [152–155].

Some alternative to the AG theory consists in developing approaches that use the configurational enthalpy as the structural parameter of the system. By now, a number of

phenomenologically augmented models have been proposed based on these approaches, which are outlined in Section 3.7.

3.7 Configurational entropy approach to glass transition

3.7.1 General remarks. The question of whether or not Planck’s formulation of the third law of thermodynamics holds for glass was one of the most discussed topics in the science of the glass transition in the 1920s–1930s (as reviewed, for example, in the books [1, 3, 4]). This discussion and the theoretical analysis of the subsequent experimental work led to the main conclusion that at the glass transition the configurational entropy of the system becomes ‘frozen-in’ at a certain level and then remains unchanged as the temperature of the body tends to absolute zero. The value of T_g —and, hence, the configurational entropy which remained as it was at this T_g —depends on the cooling rate.

Once again under active discussion in recent decades, these well-established results have been, to some extent, thrown into doubt, which renewed intensive discussions on the subject, as exemplified by the International Workshop on Glass and Entropy, Trencin, Slovak Republic (for the proceedings, see the *Journal of Non-Crystalline Solids*, **355** (2008)). No full consensus exists on the traditional view about the existence of finite entropy at low temperatures. The alternative arguments that attempt to justify a vanishing configurational entropy at the glass transition involve the concept of the continuous violation of the system’s ergodicity. As is known, however, the ergodic theory does not supply us with a foundation of the basic assumptions of statistical physics even for equilibrium systems, so its applicability to nonequilibrium systems is even more doubtful. Besides, as is shown in this review (see, for example, the model described in Section 3.8) and elsewhere, the validity of the thermodynamic approach when combined with appropriate statistical models is supported by abundant experimental evidence for the nonzero value of the configurational entropy of glass.

3.7.2 Model involving the limiting configurational entropy S_c^{lim} .

The glass transition process and the thermodynamic properties of glass require constructing the model of a glass-forming melt for their theoretical description. A simple example of such a model is considered in Refs [1, 3, 4], which also review more complex approaches to constructing such models. In current section, such models are presented and discussed.

The glass transition model developed in Refs [59, 66, 156–161] hypothesizes the existence of a limiting ‘plateau’ in the relaxation of the system for $T < T_g$, an assumption based on the DSC studies of relaxation in various materials at fixed temperatures [162, 163]. The existence of the plateau and the possible two-stage relaxation have been the topics of active discussion over the past twenty years [63–65]. In the AG theory, it is assumed that a certain intermediate metastable state exists in which the system has only a small number of accessible configurations and from which the system cannot move to a lower-energy state within the observationally accessible time scale. The evolution of the configurational entropy in this case is given by

$$S_c(t) = S_c^{\text{lim}}(T(t)) - \sum_{i=1}^n (S_c^{\text{lim}}(T_i) - S_c^{\text{lim}}(T_{i-1})) M(\xi - \xi_{i-1}), \quad (26)$$

where M is the Kohlrausch response function, ξ is the reduced time, the relaxation time is given by the Adam–Gibbs formula (23), and $S_c^{\text{lim}}(T)$ is the maximum accessible value of the

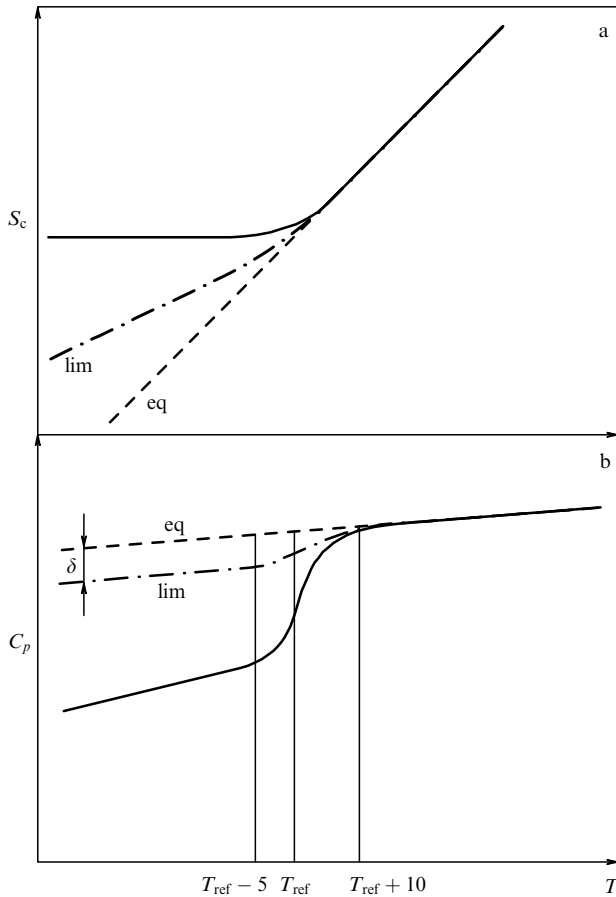


Figure 4. (a) Schematic of the temperature dependence of the configurational entropy for the liquid state (dashed line), experimental dependence for cooling (solid line), and the hypothetical dependence of the limiting state (dashed-dotted line). (b) Plot of heat capacity $C_p(T)$ in a similar notation [59].

configurational entropy. To make a comparison with experimental data, it is necessary to find the temperature dependence of the measured heat capacity, for which purpose the assumption of the equivalent entropy and enthalpy relaxations is imposed on the system. An expression for the evolution of the configurational enthalpy is obtained, from which it is an easy matter to derive an expression for C_p .

In the above-described model, an additional phenomenological parameter δ , the deviation of the metastable state from the extrapolated equilibrium state, necessarily arises (Fig. 4). More specifically, δ determines the deviation of the heat capacity from its equilibrium value C_p (for a supercooled liquid). Further still, the proposal was also made in paper [164] that the temperature T_{gd} at which the metastable state departs from equilibrium be considered as an empirical parameter. While calculations using this model give improved agreement with experimental data, no full agreement has yet been achieved for the entire range of q .

3.7.3 Hypothesis of the nonlinear configurational entropy. An alternative approach, which also relies on the configurational entropy, was developed in Ref. [165], which discusses a method (proposed in Ref. [148]) of introducing nonlinearity into the AG model and proposes an alternative version which takes into account the fact that the configurational entropy is partially frozen-in when a certain fictive temperature is reached. The expression for the total configurational entropy

then takes the form

$$S_c(T, T_f') = x_s S_c(T) + (1 - x_s) S_c(T_f'). \quad (27)$$

The authors of Ref. [165] argue that, unlike the TNM-model parameter x , which is often thermal-history-dependent, their proposed parameter x_s stands for a material property. The relations between x , x_s , T_f , and T_2 have been obtained. An efficiency comparison [166] of this and the previous model suggests the far-reaching generality of the approach using the method of the limiting configurational entropy.

3.8 Glass transition in terms of nonequilibrium thermodynamics

Instead of employing the methods outlined in Section 3.7 to describe the kinetics of glass transition, an alternative approach based on nonequilibrium thermodynamics can be applied (De Donder, van Rysselberghe [167], Prigogine and Defay [168]), which, apart from using state characterization parameters for a system in classical equilibrium thermodynamics, also introduces additional structural (or internal) order parameters for describing nonequilibrium states of the system. Glass transition treatments within this framework [1–3, 168–171] have been developed based on the ideas formulated by Bragg and Williams [172] in 1934 and by Mandelstam and Leontovich [173]. Our exposition in this review follows the thermodynamics views of Prigogine and Defay, as presented in Refs [168, 169, 174, 175].

By combining the generality of thermodynamics with the ability to use statistical physics models in determining the fine details of the processes and systems studied, the approach we present below provides, in our view, the most suitable tool for general description glass transition kinetics in various materials. The methods under discussion possess the property of flexibility, often absent or not obvious in phenomenological methods, and avoid problems currently encountered in the microscopic description of glass.

Describing glass transition (or, conversely, glass softening) along the lines of de Donder's approach requires introducing at least one additional internal parameter ξ intended to describe the transition of the system to a nonequilibrium state. Generally, ξ is different from the structural parameter ξ_{eq} in the equilibrium state. The dependence of ξ_{eq} on the thermodynamic parameters of the system is determined by considering the assumed model of the system. For example, following Refs [148, 169, 175, 176], one arrives at the simplified expression for ξ_{eq} in the form

$$\xi_{eq} = \begin{cases} g_0(T - T_0), & T_m \geq T > T_0, \\ 0, & T_0 \geq T > 0, \end{cases} \quad (28)$$

where T_m is the melting temperature. This model was developed within the framework of the hole theory of liquids [114], and the structural order parameter ξ here corresponds to the number of holes per mole of liquid. A more accurate and more practical expression for ξ_{eq} follows by considering an additional model expression for the thermodynamic potential and entropy [174], and leads to a temperature dependence of ξ_{eq} in the form of a transcendent equation given by

$$\frac{1 - \xi_{eq}}{\ln \xi_{eq}} = -\frac{1}{\chi} \frac{T}{T_m}, \quad (29)$$

with χ being a material parameter.

As the glass transition proceeds, the parameter ξ is ‘frozen-in’ at values that correspond to T_g , and which then remain unchanged as the temperature is further decreased. The glass softens as it is heated, and the parameter ξ should resume its initial value $\xi_{eq}(p, T)$.

By analogy with introducing the TNM model assumption of the response being linear in the force, the thermodynamics of irreversible processes consider a linear differential equation for the derivative $d\xi/dt$. The range of variability for ξ in some cases is conveniently written as $0 \leq \xi \leq 1$, where zero corresponds to the ordered state (crystal), and unity to a fully disordered state. The bottom line is the typical general-form equation for ξ :

$$\frac{d\xi}{dt} = -\frac{1}{\tau(p, T, \xi)}(\xi - \xi_{eq}), \quad (30)$$

where the system’s relaxation time $\tau(p, T, \xi)$ depends (due to the nonlinear nature of the glass transition) not only on the pressure and temperature but also on ξ [175]. Equation (30) is equivalent to equation (9) in Vol’kenshtein–Pitsyn’s theory but differs from it in including the dependence of τ on ξ . The applicability of such equations to the phenomenological description of relaxation process was demonstrated in the most general way by Mandelstam and Leontovich [173].

Having at one’s disposal an appropriate expression for $\tau(p, T, \xi)$, the evolution of all the thermodynamic functions of the system undergoing the glass transition can be investigated by solving equation (30). For example, the configurational heat capacity is defined by the expression

$$\Delta C_p(T) = \frac{d\Delta H(T, \xi)}{dT} \frac{d\xi}{dT}, \quad (31)$$

where the first factor can be considered a constant or can be calculated by using other approximations in combinations with the assumed model of the system. In order to describe cooling or heating of the system, the independent variable in equation (30) is changed from time t to temperature using the heating/cooling rate expression $q = dT/dt$. Then, the solution of equation (30) yields the temperature dependence of the structural order parameter in the form given in Fig. 1b. Knowing this dependence allows all required thermodynamic quantities to be calculated using appropriately chosen models. For example, by choosing an adequate model for the dependence of the configurational entropy on the structural parameter, a dependence similar to that shown in Fig. 5a can be obtained [17] for the ‘frozen-in’ configurational entropy (which remains unchanged as the system is cooled to $T \rightarrow 0$). Evidently, this simple model is consistent with the conclusion derived from a huge amount of experimental data showing that the configurational entropy is frozen-in at T_g , and that its value for $T < T_g$ is thus determined by the cooling rate.

Shown in Fig. 5b, c are the dependence of the configurational entropy S_c on the structural parameter ξ and the temperature dependence of the equilibrium value S_c^{eq} , both calculated within the hole model of the glass-forming liquid. It is seen that for the appropriately chosen model of the system, no Kauzmann paradox [84] arises and that the configurational entropy of the metastable system tends to zero only when $T \rightarrow 0$. In terms of this model, the paradox will occur only if an approximation inadequate for temperatures $T \ll T_g$ is chosen, such as the linear approximation adopted in Eqn (28) (see also Ref. [2]).

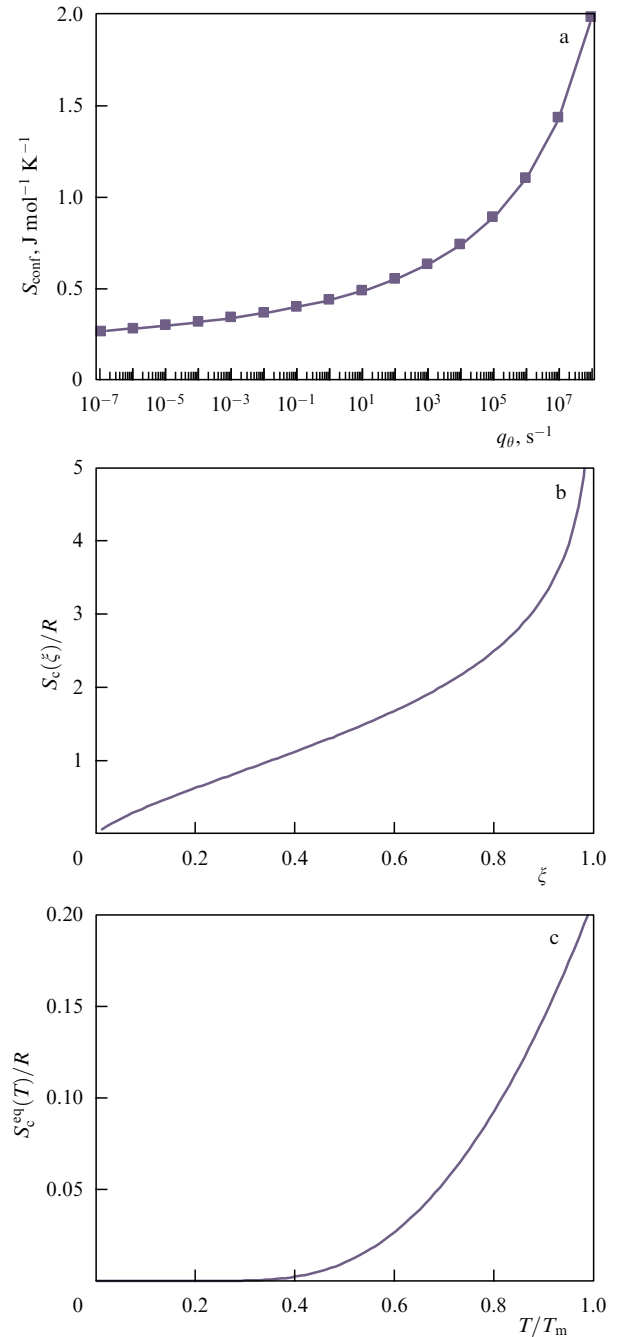


Figure 5. (a) Cooling rate dependence of the ‘frozen-in’ configurational entropy of a model system. The dependences of the configurational part of the entropy on the structural parameter ξ (b) and on the reduced temperature (c) calculated from the model expressions for S_c and ξ_{eq} [17].

Another interesting results consist in the estimate of the entropy produced in the system during its irreversible relaxation. The entropy production over the glass transition region is nonzero, similar to the case with the imaginary part of the response function at the dynamic glass transition (see Eqn (5) and Fig. 2). The results shown in Fig. 6 [17, 174] are obtained using the equation

$$\frac{d_i S}{dT} = \frac{G_{eq}^{(2)}}{qT\tau}(\xi - \xi_{eq})^2, \quad G_{eq}^{(2)} = \left. \frac{\partial^2 G}{\partial \xi^2} \right|_{\xi=\xi_{eq}}, \quad (32)$$

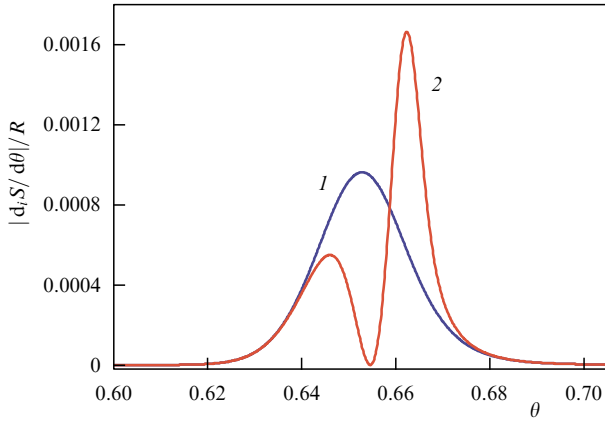


Figure 6. Entropy production in a system undergoing the glass transition and softening. $\theta = T/T_m$ is the reduced temperature. Lines 1 and 2 are for cooling and heating of the system, respectively [17].

where G is the Gibbs energy of the system. The square of the difference $\xi - \xi_{\text{eq}}$ in Eqn (32) ensures that the entropy of the system increases irrespective of how the irreversible process proceeds. The plot in Fig. 6 of the temperature dependence of the entropy production $d_i S$ in the course of the heating and cooling processes clearly shows the width of the glass transition region in thermodynamic terms. Thus, it is shown in Ref. [177] that this width is determined by the amount of entropy produced at temperature T_g during cooling. See below for more on this.

The results presented above rely on the VFT relaxation time expression (4). Fitting the simulation results to the experimental data may require various modifications of the expression for τ in equation (30). In particular, it was shown in paper [175] that an equation of the form

$$\frac{d\xi}{dt} = -\frac{\xi - \xi_{\text{eq}}}{\tau_{\text{eq}}(T)} \exp\left[-\frac{b_2}{RT}(\xi - \xi_{\text{eq}})\right] \quad (33)$$

is equivalent to the TNM model with the function of form (16) proposed by Narayanaswamy. A nonexponential form for the relaxation of the system in the Kohlrausch form is obtained by simply writing equation (30) as follows:

$$\frac{d\xi}{dt} = -\frac{1}{\tau_{\text{eq}}(p, T)} \varphi(t)(\xi - \xi_{\text{eq}}), \quad (34)$$

where $\varphi(t) = A_0^*/t^{1-\beta}$, with A_0^* being a constant [175].

The approach we have presented can be extended to cases where several structural parameters are needed to describe the state of a glass-forming system. The evolution of the system can then be described (in the linear approximation) by the system of kinetic equations in the form

$$\frac{d\xi_j}{dt} = -\sum_{i=1}^f \frac{1}{\tau_{ij}(p, T)} (\xi_i - \xi_i^{\text{eq}}), \quad (35)$$

which, by introducing the effective relaxation time of the j th structural parameter ξ_j , can be written out as

$$\frac{d\xi_j}{dt} = -\frac{1}{\tau_j^{\text{eff}}(p, T, \{\xi_i\})} (\xi_j - \xi_j^{\text{eq}}), \quad (36)$$

where

$$\frac{1}{\tau_j^{\text{eff}}(p, T, \{\xi_i\})} = \sum_{i=1}^f \frac{1}{\tau_{ij}(p, T)} \frac{\xi_i - \xi_i^{\text{eq}}}{\xi_j - \xi_j^{\text{eq}}}. \quad (37)$$

The new parameter $\tau_j^{\text{eff}}(p, T, \{\xi_i\})$ should then be substituted into the corresponding expressions, for example, the one for determining the glass transition temperature [14].

Experimentally, the glass transition process can be measured and investigated by a jumpwise change in the thermodynamic coefficients of the system, such as the heat capacity, heat expansion coefficient, and compressibility at T_g . By combining them, the well-known Prigogine–Defay ratio (an analog of the Ehrenfest relations) at the glass transition can be obtained in the following form [1, 3, 4]

$$\Pi(T_g) = \frac{1}{VT} \frac{\Delta C_p \Delta \kappa_T}{(\Delta \alpha_p)^2} \Big|_{T=T_g}, \quad (38)$$

where ΔC_p is the difference between the isobaric heat capacities of the glass-forming liquid and that of glass, while $\Delta \kappa_T$ and $\Delta \alpha_p$ are the respective differences in the isothermal compressibilities and thermal expansion coefficients. For measurements on glasses, typically, $\Pi > 1$, which differs from the Ehrenfest relations for second-order phase transitions in which the analogous parameter equals unity. The problems of how, in principle, to derive this parameter from Eqn (38) and how to obtain its values for different models are the subject of much theoretical discussion [104, 174, 178, 179]. A simplistic view of the glass transition (Simon’s model) suggests that the Prigogine–Defay ratio is always unity, provided the description of the transition utilizes only one structural order parameter and the glass transition itself is considered to be instantaneous at $T = T_g$. However, as shown, for example, in Refs [4, 179], if one takes into consideration that the glass transition occurs over a range of temperatures, then the expression for ratio (38) can differ from unity even if the system is modelled by a single structural parameter ξ . An exact expression for Π was derived in paper [18], which can be well-approximated by a relation first formulated in Ref. [174] and having the form

$$\Pi(T_g) \approx \frac{h_{p, T}}{A + h_{p, T}} \Big|_{T=T_g}, \quad (39)$$

where A is the affinity corresponding to the parameter ξ , and $h_{p, T}$ is the corresponding derivative of the enthalpy, $h_{p, T} = (\partial H / \partial \xi)_{p, T}$. The value of A in Eqn (39) should be calculated for cooling conditions, resulting in $A < 0$ and $\Pi > 1$. Values of $\Pi > 1$ can also be obtained by directly considering the thermodynamic properties of equilibrium liquid and glass. See paper [14] for various approaches to this problem. What makes these results fundamentally important is that a single structural parameter is sufficient for describing glass-forming liquids. This does not mean, of course, that this is always so, but it can be concluded that single-parameter models are quite acceptable for describing glass-forming systems.

3.9 Some current microscopic approaches to glass transition description

The development of microscopic theoretical approaches to describing the glass transition is highly topical and an actively growing area in modern glass science. Describing in statistical

physics terms the transition of a liquid into an amorphous vitreous state is a problem of ever-increasing interest, it being hoped that future theories will be advantageous in a number of respects—in particular, that in many cases no empirical parameters will be needed to make predictions. Applying the apparatus of statistical physics allows a detailed comparison to be made both with scattering experiments and with computer simulations. The reverse is also possible: experimental data (on the structural factor, for example) or the results of detailed computer simulations can be used as the basis for a subsequent, sufficiently complete simulation of various properties of a system undergoing the glass transition.

At the same time, it should be noted that the statistical theory of supercooled liquids and that of glass formation process are not yet complete, which is manifested by the fact that a correct quantitative description is not available and phenomenological corrections should be introduced into the models. Another point is that classifying the theories we present below as modern is rather vague: by modern, we mean here those which, as believed, are amenable to a great future development. The approaches described in Sections 3.1–3.8 are worked out to their full extent and cannot be improved other than by considering corrections or phenomenological expressions for some of the system's properties. Notice also that the 'microscopic' methods presented below can only be ambiguously termed so because of the mean field approximation they often use.

Sections 3.9.1–3.9.3 briefly summarize some basic ideas behind current microscopic theories of the glass transition. Detailed information can be found in specialized reviews cited in the text, where needed. Also reviewed are a number of studies which, among other direct results, simulate the heat capacity curves of a system undergoing the glass transition.

3.9.1 Energy landscape model. The employment of the system's energy landscape as a basis for simulating the glass transition and glass properties was pioneered by Goldstein [180], who was the first to indicate the importance of the energy surface topography for the dynamics of glass-forming material at low temperatures (note that the discussion of phase space structure during the glass transition dates back to Kauzmann [84]). Simulation in this case evolves on the base of qualitative—in time, hopefully, quantitative—description of the multiparticle function $\Phi(\mathbf{R})$, the potential energy of a system with a configuration as specified by the full set of position vectors $\{\mathbf{R}\}$ of its constituent particles. The behavior of a system as, for example, it is cooled down from the melting point resembles, in dynamics terms, the motion of a particle over the hypersurface Φ . Correspondingly, this expression is determined by the topography of the hypersurface $\Phi(\mathbf{R})$ which, in turn, is determined by the properties of the system (for example, by the chemical nature of its constituents). Topography can be thought of as a set of such elements as local and global minima and saddle points of various orders [181, 182]. The key concept here is the so-called 'basin' [90, 181, 182], a region in configuration space which surrounds one of the potential minima and brings the system to the state corresponding to this minimum. Clearly, a global minimum on this surface corresponds to the crystalline state; moreover, there are a large number of minima that are 'close' to it and which correspond to crystals with defects and dislocations or to polycrystals.

In addition to the minima mentioned there are, however, many other states—and these will be discussed below—that

correspond to a system structure with no long-range order, i.e., a system in an amorphous state (glass). The number of these minima increases exponentially with the number of particles N in the system. If the liquid is supercooled, then, as some of the minima become inaccessible, the function $S_c = k_B \ln N_c(T)$ decreases (N_c is the number of accessible basins). Further, the state of the system is determined by the statistical depth distribution of the minima, so that the temperature of the system determines the probability of finding the system in the basin of a given depth. In this framework, the differences between 'fragile' and 'strong' glass-forming materials can be expressed in terms of the differences in the topography of the surface $\Phi(\mathbf{R})$ [90]. It can also be shown [183] that increasing the cooling rate results in the system being 'locked' in the higher-energy basin, followed by its subsequent transition to lower-energy states, i.e., minima of the surface $\Phi(\mathbf{R})$ (structural relaxation). In this case, the dynamics of the transition are also determined by the topography of $\Phi(\mathbf{R})$.

One approach [153, 184] to simulating the glass transition of the system consists in modeling the landscape of the free energy $\Phi(T, V, N, \{\mathbf{R}_i\})$. The probability of finding the system in a certain configuration $\{\mathbf{R}_i\}$ is then given by

$$P(\{\mathbf{R}_i\}) = \frac{\exp[-\beta\Phi(T, V, N, \{\mathbf{R}_i\})]}{Z(T, V, N)}, \quad (40)$$

where Z is the partition function of the system. The expectation value of a certain physical quantity A is, by definition, the integral of the product AP over all configurations $\{\mathbf{R}_i\}$. Hence, the derivative of A with respect to temperature is partly determined by the topography of the surface Φ . For example, Ref. [184] examines the entropy and heat capacity of the system:

$$C = \left\langle T \frac{\partial S(\{\mathbf{R}_i\})}{\partial T} \right\rangle + \frac{1}{k_B T^2} \langle \Delta E(\{\mathbf{R}_i\})^2 \rangle, \quad (41)$$

where $\Delta E(\{\mathbf{R}_i\}) = E(\{\mathbf{R}_i\}) - \langle E \rangle$, and E is the energy of the system in the configuration $\{\mathbf{R}_i\}$, and uses a simple model as an example to demonstrate the significance of the second term in Eqn (41) in the description of experiments. The study of the dynamic properties of the system requires introducing an additional probability function to take into account the initial and final configurations of the system. The dynamics of Φ for a simple model is considered in Ref. [185], whereas another approach is studied in Refs [186–189]. Calculations of the evolution of heat capacity curves were performed for model systems in Refs [190–194]. Reference [194], in particular, reported the dependence of the glass transition temperature on the cooling rate. References [62, 195] calculate the evolution of the heat capacity of polystyrene and polymethyl methacrylate (PMMA) with a model corrected by introducing a temperature-dependent Φ . Reference [196] discusses the general aspects of the temperature dependence of the relaxation time by applying the energy landscape models to polymers.

A series of studies [197–199] present a model allowing one to calculate the enthalpy hypersurface for describing the glass transition in selenium. At high temperatures, the system is easy to move between various basins of the hypersurface H , but upon cooling such transitions between different structures (basins) become rarer until finally the system in the glassy state turns out to be 'locked' in a phase subspace. The

probability for the system to assume a given configuration (to occupy a given basin) is determined by an expression analogous to formula (40). The dynamics of the enthalpy landscape is described by a set of differential equations (whose number is equal to the number of basins in H), their coefficients being determined by the thermal history and the theory of transition states. In Refs [197–199], an exact calculation of the function H for a system of a small number of particles was performed using *ab initio*-calculated interatomic potentials for selenium, providing the description of the evolution of the molar volume, thermal expansion coefficient, and viscosity of a system under cooling.

3.9.2 Mode-coupling theory. One of the popular theories that have been developed in recent decades to describe the dynamics of supercooled liquids is the mode-coupling theory (MCT), first proposed independently in Refs [200] and [201]. At the basis of MCT lies the equation of motion for the dynamic structure factor $F(k, t)$ of a one-component liquid:

$$\frac{d^2 F(k, t)}{dt^2} + \frac{k^2 k_B T}{mS(k)} F(k, t) + \int_0^t d\tau M(k, \tau) \frac{d}{dt} F(k, t - \tau) = 0. \quad (42)$$

The exact description of the dynamics of the system requires the specification in equation (42) of the quantities $M(k, \tau)$, the memory kernel for particles of a given mass at a given temperature, and $S(k) = F(k, 0)$, the static structure factor. The fundamental assumption of MCT is the closure in the expression for $M(k, \tau)$ to the autocorrelation density functions $F(k, t)$ written in a quadratic form [201]. Thus, knowing the specific dependence $S(k)$ for the liquid under consideration, numerical methods can be applied to solve equation (42). An important prediction of MCT is the value of the critical temperature T_c at which the self-diffusion coefficient becomes zero or, in other words, an infinite increase is observed in the α -relaxation time of the correlation functions:

$$D \sim \frac{1}{\tau} \sim (T - T_c)^\gamma, \quad (43)$$

where the exponent $\gamma > 3/2$. This prediction has been tested repeatedly in many experiments and computer simulations, and it has been shown that in some systems D and τ follow different power laws. It is also shown in paper [202] that D cannot become zero (this dependence is an artifact of the idealized MCT).

Of interest is the character of the time dependence of the reduced correlation function $\Phi(t) = F(k_0, t)/S(k_0)$ (see Fig. 7). There are three regimes which can be recognized

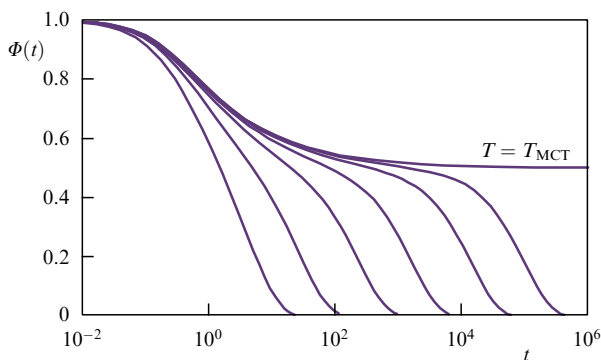


Figure 7. Time evolution of the correlation functions $\Phi(t)$ according to MCT for different temperatures [204, 206].

for different temperatures: the initial fast relaxation to a plateau which is determined by the value of k_0 ; the slow relaxation near the plateau, and the β -relaxation and structural α -relaxation.

The explanation for this behavior of $\Phi(t)$ is that over a short period of time the particle moves ballistically, but then the particle turns out to be ‘locked’ in a ‘cage’ of its nearest neighbors. It is not until some time later, when the β -relaxation is completed, that the particle leaves the cage. Yet another prediction of MCT is the superposition principle for α -relaxation:

$$\Phi(t) = \Psi\left(\frac{t}{\tau(T)}\right), \quad (44)$$

i.e., correlations for different temperatures can be reduced to a single curve by plotting them on the t/τ scale. Also of interest is the fact that the MCT prediction for Ψ in Eqn (44) corresponds to the Kohlrausch formula.

A characteristic feature of the so-called idealized MCT model, the low temperature behavior of correlation functions plotted in Fig. 7, does not fit the reality. An extended version of MCT considers the possibility of activation processes accompanied by a particle hopping between the ‘cages’. Thus, Ref. [203] shows that such an approach restores the ergodicity of the system at and below T_c . Some details of MCT are reviewed in Refs [87, 204–207].

Overall, despite some limitations and disadvantages, MCT is an effective analyzing tool for glass-forming materials, providing general insights based on microscopic interaction potentials between the atoms and molecules of the system under study [208].

3.9.3 RFOT theory. The work of Kirkpatrick, Thirumalai, Wolynes, and others over the last few decades has resulted in a new microscopic approach, which its authors called the Random First-Order Transition (RFOT) theory [209–211] and which is, in fact, the application of a similar previously developed theory of transitions in model spin systems [11, 212] to the glass transition [213, 214]. In the development of their approach, the authors also heavily relied on the Adam–Gibbs theory, MCT, and the energy landscape model.

The term ‘random first-order transition’ is meant to refer to the freezing of a liquid and its conversion to a number of aperiodic structures (quasicrystals), a point which sets this transition fundamentally apart from first- and second-order phase transitions. The authors of Refs [209–211] note the existence of two temperatures which determine the glass transition behavior of the system. For a temperature T below the dynamic transition temperature T_A , it can be shown in the mean field approximation that part of the phase space of the system is a set of a large number of potential ‘wells’ corresponding to the statistically equivalent amorphous states (similar to Goldstein’s theory, the number of such states increases exponentially, $\sim \exp(\alpha N)$, where N is the number of particles in the given region of the system).

For $T < T_A$, the displacements of molecules in a liquid are primarily determined by activation processes, leading to the ‘stratification’ of the system and to its transformation into a mosaic-like system of ‘drops’ in various amorphous states (as in the AG theory, the size of these regions is characterized by the correlation length ξ). The authors of the RFOT theory followed the analogy with the classical theory of nucleation [215–217] in taking into account the difference in the

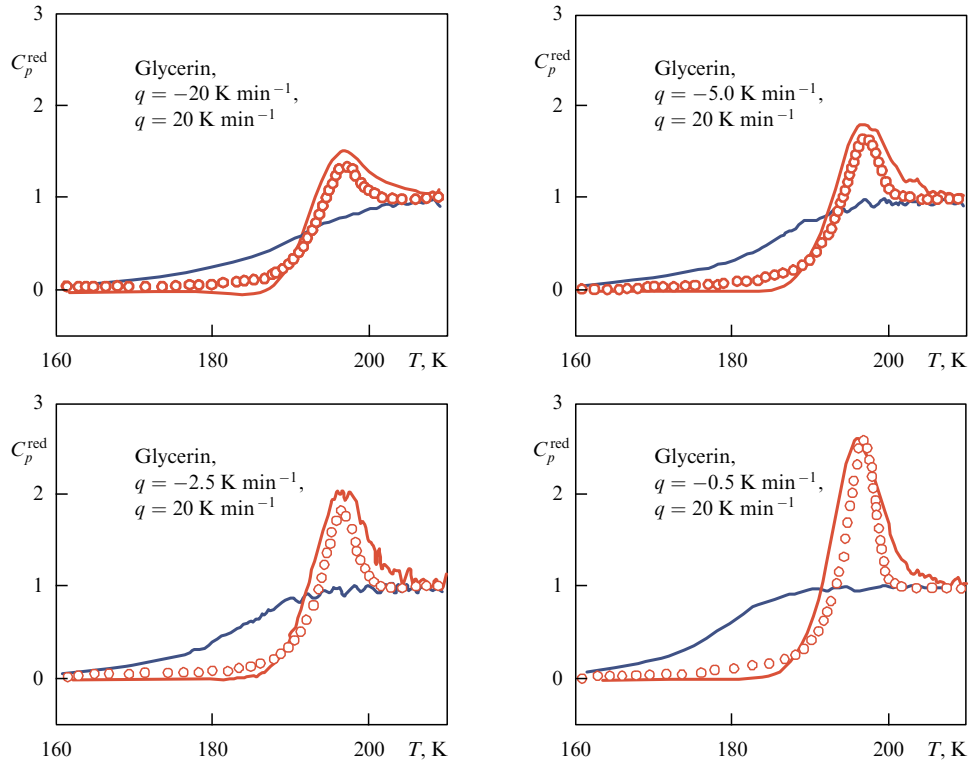


Figure 8. (Color online.) RFOT/MCT simulation of temperature curves C_p^{red} [see Eqn (8) in the text] for glycerin for different cooling rates q marked in panels [223].

rearrangement due to the phase interface in the system (which is where this theory differs from the AG theory). However, whereas in the nucleation process (which leads to a first-order phase transition) the formation of a sufficiently large number of particles in the new phase causes a fast growth of clusters at a given temperature, the tessellation model of a cooled liquid allows the formation of a new ‘drop’ of the amorphous phase within the already existing larger ‘drop’. This leads to the formation of a system of clusters that are in the process of continuous rearrangement and whose size increases only with decreasing temperature according to the law

$$\xi \sim \frac{1}{(T - T_K)^{2/d}}. \quad (45)$$

The temperature T_K in formula (45) is the temperature of a random first-order phase transition (to the state of ‘ideal’ glass), a temperature at which the configurational entropy determining the transition between amorphous states becomes zero. The divergence in formula (45) is stronger than in the Adam–Gibbs theory, a fact which in some systems should result in the amorphous clusters becoming nanometer sized. The RFOT theory formulated in this way, as well as the AG model, is currently associated in a certain sense with the discovery in glass-forming systems of nontrivial spatio-temporal fluctuations of a comparable size, called dynamic heterogeneities [206, 218, 219]. Over the last twenty years, much experimental, theoretical, and computer simulation work has been done to study these heterogeneities [206, 218, 220]. Some studies, though, have cast doubt on the existence of this effect in molecular liquids [221, 222].

An example of the application of the RFOT theory (in combination with MCT) to glass formation kinetics is given in Ref. [223], which yields the expression for the mobility field

$\mu(x, t)$ of a typical form employed in the system of equations for the fictive temperature:

$$\frac{\partial T_f}{\partial t} = -\mu(T_f - T).$$

Reference [223] simulates the heat capacity curves for glycerin and three other glass-forming materials for different heating and cooling rates (Fig. 8). This work also shows that the theory under review produces a bimodal distribution of relaxation times for a polymer (polystyrene) at structural relaxation at temperatures well below T_g .

Overall, we note that, although the RFOT theory, which is a conglomerate of various theories, is advantageous in making many analytical predictions, it remains disadvantageous in some respects and also leads to new problems, such as the description of the transition from the dynamical slowing-down in the MCT regime to the state involving the proceeding of activation processes.

4. Kinetic criteria of glass transitions

4.1 General kinetic criterion of glass transition and examples of its application

Establishing the dependence of glass properties on the heating or cooling rate is important for practical applications. Furthermore, the very fact of the existence of this dependence is fundamentally important for the correct description of the glassy state and the glass formation process. The Bartenev–Ritland law, Eqn (3), is the first result in this area [20, 22]. In a subsequent paper [176], a similar analysis by Moynihan confirmed the experimental validity of this law for three different glasses and also stated that the law applies in general to glass-forming systems. A similar statement was

recently made by Mazurin [224]. A detailed analysis of the problem was carried out in monograph [1], and Refs [17, 18, 225] present numerical simulations for a wide range of cooling and heating rates.

In paper [19], a general kinetic criterion of glass transition is formulated for the case of a temperature variation, as well as of other external control parameters generalizing, in particular, earlier work in this direction. The glass transition, i.e., the kinetic transition of a system from equilibrium state to nonequilibrium, can be described in a general way in the framework of the thermodynamics of nonequilibrium processes by adding a set of state parameters $\{\xi_i\}$ to the usual properties of the system. When the system requires no more than one structural parameter ξ to describe its nonequilibrium state, the kinetics of the change in this parameter under isothermal conditions is described in a general way by an equation of the form (30). If the system is heated or cooled at a fixed rate q , then one can write the following equation

$$\frac{d\xi}{dT} = -\frac{1}{q\tau(p, T, \xi)} (\xi - \xi_{\text{eq}}), \quad q = \frac{dT}{dt}. \quad (46)$$

By introducing the characteristic time for variation in temperature τ_T , the change in the temperature of the system can be written in a form similar to Eqn (30):

$$\frac{dT}{dt} = -\frac{1}{\tau_T} T, \quad \tau_T = \frac{T}{|q|}. \quad (47)$$

We can use the relation between times τ and τ_T to consider the stages a liquid goes through in the process of glass transition under cooling (or in the reverse process). Clearly, the system can remain in a state of thermodynamic equilibrium if $\tau \ll \tau_T$, whereas, in the opposite extreme, $\tau \gg \tau_T$, the state of the system is ‘frozen-in’, meaning that the glass transition is completed. Hence, the glass transition interval is determined by the relation $\tau \sim \tau_T$, i.e., the characteristic times for the relaxation of the system and for temperature change are of the same order of magnitude. Thus, we have arrived at a general formulation of the kinetic glass transition criterion. With this criterion, the expression for the glass transition temperature can be written as [14, 19]

$$\tau \approx \tau_T, \quad \left(\frac{1}{T} \left| \frac{dT}{dt} \right| \tau \right) \Big|_{T=T_g} \approx C, \quad C \approx 1. \quad (48)$$

The selected value of C in Eqn (48) should remain unchanged when determining T_g for various cooling or heating rates. The expression $\tau \sim \tau_T$ can be applied in the general form to the glass transition when other properties of the system, for example, pressure, are varied, or it can be used to determine the temperature of the dynamic glass transition.

Clearly, expression (48) can be approximated by $(|q|\tau_R)|_{T=T_g} = \text{const}$ (according to Bartenev’s proposal [20, 21]) or by using Maxwell type relaxation processes in the form of the Bartenev–Ritland law (3). It is also possible, however, to obtain a generalized Bartenev–Ritland law, for example, the relationship

$$\frac{1}{\tilde{T}_g - \tilde{T}_0} = \ln \tilde{T}_g^2 - \ln \tilde{q}, \quad (49)$$

if VFT relaxation is assumed. Equation (49) uses the reduced values of the temperature and cooling rates [19, 177]. Expression (49), whose right-hand side is seen to directly depend on T_g , suggests that for certain values of the cooling

rate q the behavior of T_g deviates from that given by the original expression of the Bartenev–Ritland law in the form of Eqn (2) (see Section 4.2 for details).

From Eqn (48) also follows an expression for the change in the glass transition temperature T_g as a function of other system parameters, for example, pressure [14, 19]:

$$\frac{dT_g}{dp} = -\frac{(\partial\tau/\partial p)_T + (\partial\tau/\partial\xi)(\partial\xi/\partial p)}{(\partial\tau/\partial T)_p - \tau/T} \Big|_{T=T_g, p=p_g, \xi=\xi(T_g, p_g)}. \quad (50)$$

Hence, determining the derivative dT_g/dp requires knowing the dependences $\tau(p, T, \xi)$ and $\xi(p, T)$. Formula (50) is readily extended to the case of several structural parameters $\{\xi_i\}$ [14]. In the simplest case, various expressions can be obtained for dT_g/dp by neglecting the pressure dependence of the structural order parameters and using different models for $\tau(p, T)$. Like Ehrenfest’s theory of second-order phase transitions, here we do not have two equations that are always applicable for dT/dp , but only one general equation, Eqn (50). Hence, the pressure dependence of the glass transition temperature does not allow us to conclude that the Prigogine–Defay ratio is equal to unity [14, 19].

Assuming linearity between the relaxation time and the viscosity of the liquid (which is true for many glass-forming materials), we can derive an expression for determining η at the glass transition temperature [14, 17, 18]:

$$\log \eta(T_g) \approx B - \log |q|, \quad (51)$$

where the parameter B is weakly dependent on T_g . It follows that Tammann’s [24] popular and widely used glass transition criterion assigning a definite value of viscosity to T_g does not apply to a wide range of heating (cooling) rates used in the process. Given the rate, the value of viscosity at the glass transition can be calculated by Eqn (51), where the temperature T_g is determined from the general criterion (48).

As an example of the application of criterion (48) to the dynamic glass transition, let us consider the relaxation of a system under the condition where the external parameter (temperature) oscillates with frequency ω . The equilibrium value of the structural parameter in Eqn (46) varies as $\xi_{\text{eq}} \sim \exp(i\omega t)$. But then, by considering the characteristic time $\tau_D = 1/\omega$ for the change in the equilibrium value ξ_{eq} , we can obtain a typical criterion (denoted frequently as Frenkel–Kobeko relation [3, 4]) of the form $\omega\tau \sim C$, where $C \sim 1$ [19, 20]. In order to arrive at the same value of T_g at thermal and dynamic glass transitions (determined via the Frenkel–Kobeko relation) the condition $q/(T\omega) = C \approx 1$ must be fulfilled [114, 226].

Knowing the evolution of the structural parameter ξ and taking into account the evolution of p and T makes it possible to calculate the evolution of any other property of the system. Assuming that one of the system parameters, φ_m , is nonlinear in ξ , $\varphi_m \propto (\xi - \xi_{\text{eq}})^m$, and using the Kohlrausch form for the relaxation of ξ , namely

$$\frac{\xi(t) - \xi_{\text{eq}}}{\xi(0) - \xi_{\text{eq}}} = \exp \left[-\left(\frac{t}{\tau} \right)^\beta \right], \quad \beta < 1, \quad (52)$$

the relaxation of φ_m is readily expressed as [14]

$$\ln \varphi_m(t) = \ln \varphi_m(0) - \left(\frac{t}{\tau^{(m)}} \right)^\beta, \quad \tau^{(m)} = \frac{\tau}{m^{1/\beta}}. \quad (53)$$

Hence, it can be concluded that different thermodynamic properties of a system may have different relaxation times, i.e., the calculated values of the glass transition temperature T_g depend not only on the material under study or the rate of change of the external parameter but also on the specific property which is being determined in the experiment. Further, assuming that the relaxation time of the parameter ζ is described by the VFT law (4) and using criterion (48), we can obtain the modified Bartenev law

$$\frac{B}{T_g - T_0} = \log \frac{T_g}{\tau_0} - \log |q|. \quad (54)$$

Similarly, for the property φ_m , making the replacement $\tau_0 \rightarrow \tau_0/m$, we have

$$\frac{B}{T_g^{(m)} - T_0} = \log \frac{T_g^{(m)}}{\tau_0} + \log m - \log |q|. \quad (55)$$

Equations (54) and (55) express the behavior of the glass transition temperatures obtained by various methods for different cooling rates of the system. It is seen that the value of m determines the difference between T_g and $T_g^{(m)}$ for equal values of q .

4.2 Width of a glass transition range

The approach described in Section 4.1 can be applied to the general analysis of the glass transition width as a function of the heating or cooling rate of the system [177]. For the temperatures characterizing the boundaries of the glass transition interval, we can write

$$\begin{aligned} T_g^+ : \left(\frac{1}{T} \left| \frac{dT}{dt} \right| \tau \right) \Big|_{T=T_g^+} &\approx \alpha^+ \ll 1, \\ T_g^- : \left(\frac{1}{T} \left| \frac{dT}{dt} \right| \tau \right) \Big|_{T=T_g^-} &\approx \alpha^- \gg 1. \end{aligned} \quad (56)$$

The glass transition width depends on the choice of the parameters α , which fully corresponds to the methodological features of any its experimental or theoretical definition [110]. Using relations (56), one can obtain analytical expressions for the glass transition width for systems whose relaxation is expressed by two widely employed laws, the Arrhenius law and VFT phenomenological equation.

Let us write the Arrhenius law in the form

$$\tau = \tau_0 \exp \frac{U_0}{RT} = \tau_0 \exp \frac{A}{T}, \quad \tau_0 = \frac{h}{k_B T}. \quad (57)$$

Then, by substituting the expression for $\tau(T)$ into Eqns (48) and (56) and introducing the dimensionless variables for the temperature and temperature change rate, viz.

$$\tilde{T} = \frac{T}{A}, \quad \tilde{q} = \frac{h}{k_B A^2} \left| \frac{dT}{dt} \right|, \quad (58)$$

the relation for the glass transition temperature \tilde{T}_g can be written as

$$\frac{1}{\tilde{T}_g} = \ln \tilde{T}_g^2 - \ln \tilde{q}. \quad (59)$$

Noting that the logarithm of the square of the reduced glass transition temperature varies much more slowly than the

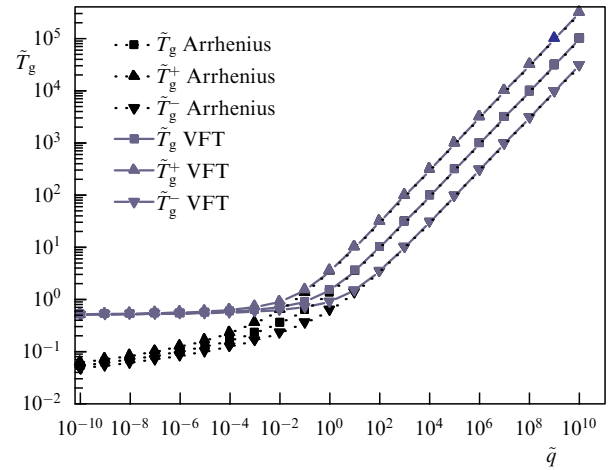


Figure 9. (Color online.) Comparison of characteristic reduced temperatures of the glass transition interval as a function of the cooling/heating rate for the Arrhenius (dark lines) and VFT (blue lines) relaxation times [177].

logarithm of q , expression (59) is an analog of Bartenev's glass transition law.

For the glass transition boundaries, we similarly find

$$\begin{aligned} \frac{1}{\tilde{T}_g^+} &= \ln [(\tilde{T}_g^+)^2 \alpha^+] - \ln \tilde{q}, \\ \frac{1}{\tilde{T}_g^-} &= \ln [(\tilde{T}_g^-)^2 \alpha^-] - \ln \tilde{q}. \end{aligned} \quad (60)$$

Using Eqns (59) and (60) with the specified values of α^\pm , it is possible to investigate analytically T_g and the glass transition interval width as a function of the cooling rate q over its entire range. The curves of the glass transition temperature and glass transition interval boundaries are shown in Fig. 9 for a wide range of q .

Introducing similar reduced quantities

$$\tilde{T} = \frac{T}{B}, \quad \tilde{T}_0 = \frac{T_0}{B}, \quad \tilde{q} = \frac{h}{k_B B^2} \left| \frac{dT}{dt} \right|, \quad (61)$$

for the Vogel–Fulcher–Tammann relaxation law (4), the dimensionless glass transition temperature and the upper and lower boundaries of the glass transition interval can be expressed as [177]

$$\begin{aligned} \frac{1}{\tilde{T}_g - \tilde{T}_0} &= \ln \tilde{T}_g^2 - \ln \tilde{q}, \\ \frac{1}{\tilde{T}_g^+ - \tilde{T}_0} &= \ln [(\tilde{T}_g^+)^2 \alpha^+] - \ln \tilde{q}, \\ \frac{1}{\tilde{T}_g^- - \tilde{T}_0} &= \ln [(\tilde{T}_g^-)^2 \alpha^-] - \ln \tilde{q}. \end{aligned} \quad (62)$$

The first expression in Eqn (62) is (with the above reservations) the modified Bartenev–Ritland equation for the VFT relaxation law. How the relaxation law affects the glass transition temperature can be assessed by comparing the dependences obtained from Eqns (59), (60), and (62) (see Fig. 9). It is seen that differences already appear at sufficiently low cooling/heating rates, i.e., when the glass transition occurs at temperatures sufficiently close to T_0 . A comparison of

analytical calculations and numerical simulations using Eqn (46) [177] shows that, for the dependences to be identical, it is necessary to select such values of α^+ and α^- that are probably determined by the parameters of the relaxation law and by other properties of the simulated system.

The glass transition width can also be estimated in an alternative way to that described above by employing only the general thermodynamic expressions for the properties of a system undergoing a glass transition. We can take the dependence of the entropy production in the system as the basis for this: it is seen from Fig. 6 that outside of the glass transition interval it is zero, allowing this quantity to be used for deriving expressions for ΔT_g . The position of the maximum of $d_i S$ under cooling can then be considered as the thermodynamic definition of the glass transition temperature, and the width of the interval is determined by Taylor expanding $d_i S/dT$ [177]. As a result, describing the relaxation by equation (46), the following estimates may be obtained:

$$T_g \approx \left[\frac{d}{dT} \ln \frac{(\xi - \xi_{eq})^2}{\xi_{eq}} \right]^{-1}, \quad (63)$$

$$T_g^+ - T_g^- = 2 \left\{ -\frac{1}{2} \frac{d^2}{dT^2} \left[\ln \frac{1}{q\tau} \frac{(\xi - \xi_{eq})^2}{\xi_{eq}} \right] \Big|_{T=T_g} \right\}^{-1/2},$$

which can be used to directly calculate the glass transition temperature and the glass transition interval width for systems with a single structural parameter (assuming the temperature dependences of ξ , ξ_{eq} , and τ are known).

5. Physical relaxation of polymers

The structural relaxation of glass-forming liquids and polymers represents a kinetic process which is currently of topical interest from both a fundamental perspective (description of the glass transition process) and for a variety of applications. The fact that materials dynamically change their properties (for example, viscosity) when stored or used at a given temperature is important for high technology applications of polymers or, for example, in the food industry. The relaxation effect itself has been known since the work of Kohlrausch around 1876, then with renewed interest in 1930s [97] and came under research scrutiny about 50 years ago [32]. Presently, experimental methods for observing the physical relaxation of polymers are sufficiently large in number, and most efforts in this field are directed to studying changes in volume or enthalpy [227, 228]. The subject matter of this section includes the simulation of experimental data and research prospects in this field.

Early work on relaxation was focused on the temperature range $T \geq T_g$, because the relaxation time of the system at these temperatures is sufficiently short (on the order of seconds). The temperature dependence of the relaxation time is determined either by the Arrhenius law or by the VFT equation, depending on the system. The experimental data demonstrate well the nonlinear and nonexponential nature of glass transition relaxation. Naturally, we need methods ensuring corresponding properties to be able to conduct simulation studies.

A number of simple but adequate semiempirical expressions for the dependence of the integral characteristic curves C_p (for example, for the enthalpy) on relaxation temperature and time can be found in Refs [162, 229, 230]. These references

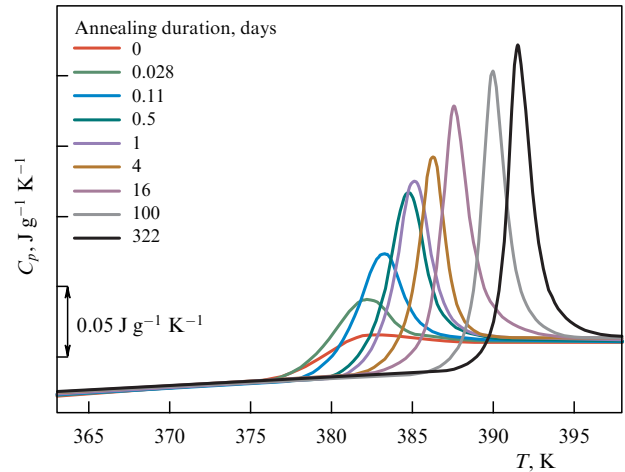


Figure 10. (Color online.) Example of heat capacity measurements in polystyrene during heating following relaxation at different time intervals [65].

allow the conclusion that the structure of a polymer affects the relaxation process. At the same time, the full description of the curves $C_p(T)$ requires a different approach. The application in this case of TNM or similar methods suggests that the experimental relaxation (‘aging’) interval of the polymer is divided into intervals, whose number is taken to be large enough to secure the required simulation precision. The simulation is carried out for heat capacity curves under heating, which are subsequently compared with their experimental counterparts (Fig. 10). These curves are then either considered directly as modeling the experimental data or used to obtain integral characteristics whose dependence on the relaxation temperature and time is being investigated.

Overall, there are three stages in the simulation of experiment: (1) initially, the liquid is cooled to a specified temperature T_a at a specified rate; (2) the liquid relaxes for a specified period of time t_a , and (3) the liquid is heated at a fixed rate q . The measurement and simulation of the relaxation kinetics in various polymers are detailed in a series of references [57, 58, 129, 231, 232] (see also review [61]). Some of the model parameters (for example, Δh^*) were determined from the characteristic behavior of measured quantities, and others by a least-mean-square fit of the model results to the experimental data. It is shown that the TNM and AG models reproduce rather well the heat capacity curves of polymers heated following relaxation; on the other hand, the parameters of the method are found to be manifestly dependent on the thermal history of the experiment—in particular, the parameters x and β should be varied when T_a is changed by 10 K or more or when t_a is changed by an order of magnitude or more.

Detailed studies of the relaxation of polyetherimide were performed in Refs [233, 234]. In Refs [59, 159], data on polystyrene and three of its derivatives are described within the model of limiting configurational entropy. That the data turn out to be fitted better than by TNM is expected due to the added parameter. Importantly, even varying T_a by 20 K and t_a between 300 and 1000 min did not produce full agreement with experimental data. A subsequent study [158] on polystyrene-based mixtures estimated the size of inhomogeneities as a function of the mixture composition. Reference [235] compared the relaxation kinetics of the volume and entropy of polystyrene at temperatures close to T_g . In the neighbor-

hood of the glass transition temperature, their behavior is the same, but extrapolation to the region $T_g - 20$ K should lead to differences according to the authors. At the same time, similar experiments in Ref. [236] show that the relaxation of volume and enthalpy are of the same nature and have the same parameters.

Over the last five years, most discussion in this area has been concerned with the relaxation mechanism we described in the Introduction, a two-stage mechanism, so called due to the intermediate state ('plateau') present between the glassy and liquid states (see Fig. 3). In some early studies [59, 230], similar hypotheses were suggested based both on experimental data and simulation results, but it is only in 2011 that such observations were made directly in an experiment [63]. In subsequent work, some groups refuted [64], whereas others [65] improved—and hence confirmed—these results. It should be noted that these results were obtained by only one group of researchers [63, 65, 227] and have not yet been confirmed independently. Because a single experiment in this field takes over a year to complete, it is expected that in the next one or two years new data will be obtained which will enable a more definitive conclusion to be drawn. Anyway, this research holds great promise for the development of the theory of the glass transition, as does the simulation of the two-stage relaxation process from the fundamental standpoint.

6. Glass transition kinetics in a wide range of cooling rates

Along with the study of physical relaxation, the kinetics of the polymer glass transition under linear variation of temperature over a given range are being investigated, and a rather large amount of literature has accumulated. Zhurkov and Levin [109] were the first to observe a peak in the temperature dependence of the heat capacity of polyvinyl acetate and polymethyl methacrylate at two different heating rates. The dependence of the glass transition temperature as described by Bartenev [21] is also well manifested in polymers [21, 109, 113]. Subsequent decades have witnessed the gradual extension of the range of accessible cooling rates and an increase in measurement precision. As new theories of glass transition kinetics appear, their potential in relation to experimental data is continuously examined [57, 147, 151, 232, 237–243].

Recent years have seen a renewal of activity in this field due, in particular, to the ability of modern DCS instruments to vary the cooling rate over a very wide range. As a result, the existing glass transition models have been verified and alternative approaches proposed. Measurements of the dependence of the glass transition temperature of polystyrene on the cooling rate are presented in Refs [244, 245]. Reference [246] investigated the glass transition of polystyrene over the widest cooling rate range ever reported ($5 \times 10^{-6} - 2 \text{ K s}^{-1}$).

Figure 11 demonstrates the characteristic experimental curves and simulation results in the form of the values of the heat capacity C_p^{norm} equal to the difference of two reduced heat capacities, one of which is measured under heating at a rate of 0.5 K s^{-1} following cooling at an indicated rate taken from the given interval, and the other at heating at 0.5 K s^{-1} following cooling at 0.5 K s^{-1} (this measurement scenario is needed to improve the quality of the resulting curves at sufficiently slow cooling). Modeling the full set of curves first using the TNM and AG models and then in the

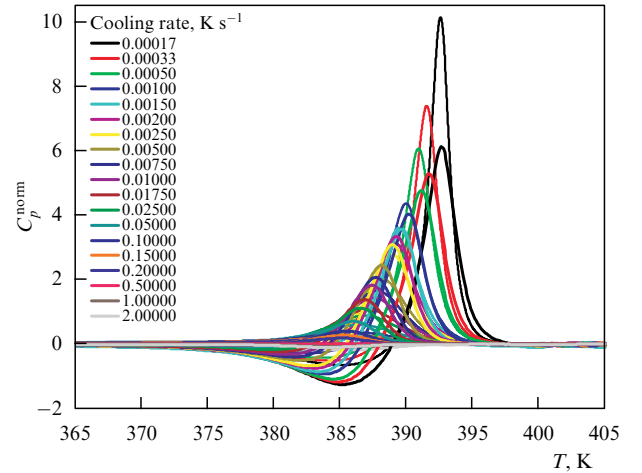


Figure 11. (Color online.) Temperature dependence of the heat capacity of polystyrene for different cooling rates as measured under heating at a rate of 0.5 K s^{-1} and the model data [246]. Thick lines — experiment, and thin lines — Adam–Gibbs simulation.

framework of nonequilibrium thermodynamics (see papers [174, 177]) with the same parameter set yields qualitatively similar results (see Fig. 11).

To perform the TNM simulation, expression (18) is modified by noting that polystyrene belongs to the class of hard glass-forming systems, so one has

$$\tau(T, T_f) = \exp \left[\ln \tau_0 + \frac{\Delta h^*}{R(T - T_0)} x + \frac{\Delta h^*}{R(T_f - T_0)} (1 - x) \right]. \quad (64)$$

The Adam–Gibbs theoretical approach implies the specification of the dependence $\Delta C_p(T)$ for the system under study. Review [61] suggests a number of expressions (a constant, and linear and hyperbolic dependences), each of which was used to calculate the model curves in Ref. [246]. The best agreement with experiment was achieved with the linear dependence $\Delta C_p(T) = C_0 + C_1 T$, which, when substituted into Eqns (23) and (25), yields

$$\tau_{\text{AG}}(T, T_f) = \tau_0 \exp \left\{ \frac{A}{RT [\ln(T_f/T_2) + C(T_f - T_2)]} \right\}. \quad (65)$$

Finally, while a number of expressions for τ were tested for the purpose of a description in the framework of nonequilibrium thermodynamics (see Section 3.8), the best agreement with experiment was obtained with a new expression, which combines the VFT law and formula (23) from the AG theory:

$$\tau(\theta, \xi) = \tau_0 \exp \left\{ \frac{B}{R(\theta - \theta_0)} - \frac{A}{R\theta [\ln(1 - \xi) + \xi \ln \xi / (1 - \xi)]} \right\}, \quad (66)$$

where θ is the reduced temperature, the first term in the exponential is the VFT law, and the second term is determined, according to the AG theory, by the configurational part of the entropy of the system.

It can be concluded that, given such a wide range of heating/cooling rates q , none of the methods can provide a sufficient accuracy in describing experimental data. A point to note in Fig. 11 is that discrepancies occur not only in the

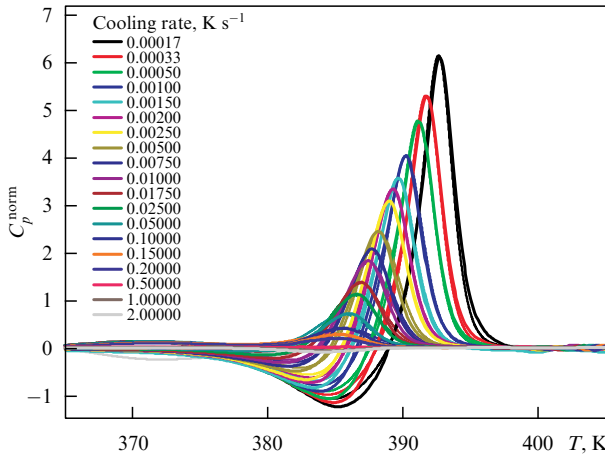


Figure 12. (Color online.) TNM simulation of isobaric heat capacity curves by varying the Δh and β parameters for each measurement (heating or cooling) [246]. Thick lines — experiment, and thin lines — Narayanaswamy's simulation.

high C_p peaks corresponding to slow cooling and, hence, to the parallel existence of structural relaxation, but also at relatively large rates, for which lower-than-measured heat capacity peaks are predicted.

Reference [246] argues, consistent with previous understanding, that the exact simulation of the curves can be achieved only by varying a certain two of the method's parameters (for example, Δh and β) at a variable rate q . That is, if for each curve $C_p(T)$ —and, notably, for heating and cooling separately, because the absolute values of the rates are different—one automatically chooses two parameters and leaves the others fixed, then a qualitative agreement between the theoretical and experimental curves can be achieved for most of the methods discussed in Section 2. Results of such calculations, conducted by twenty experimental curves (nineteen for cooling and one for heating) are presented in Fig. 12. The small shape differences between the model curves (especially near the minimum of C_p) are constant for different values of the cooling rate q and, hence, can be viewed as a drawback of the simulation method or as a specific feature of the glass transition in polystyrene.

There are two factors qualitatively supplementing the analysis of the fit between the model and measured curves, namely, the descriptive behavior characteristics of the curve parameters such as, first, the position and value of the C_p maximum and, second, their integral characteristics, the limiting fictive temperature T_f' proportional to the integral of the enthalpy H :

$$T_f' = T_f^0 - \frac{\Delta H}{\Delta C_p}, \quad (67)$$

where T_f^0 is the reference value of the fictive temperature determined by Eqn (6) from an individual measurement of C_p under heating and cooling at the same rate of 0.5 K s^{-1} [246]. It is shown that the TNM model yields better agreement with the experiment for the positions of the heat capacity peaks, whereas the AG method performs better for the values of C_p peaks.

Figure 13 compares the dependence of the limiting fictive temperature on the cooling rate q for different simulation methods. It is seen that when using a single set

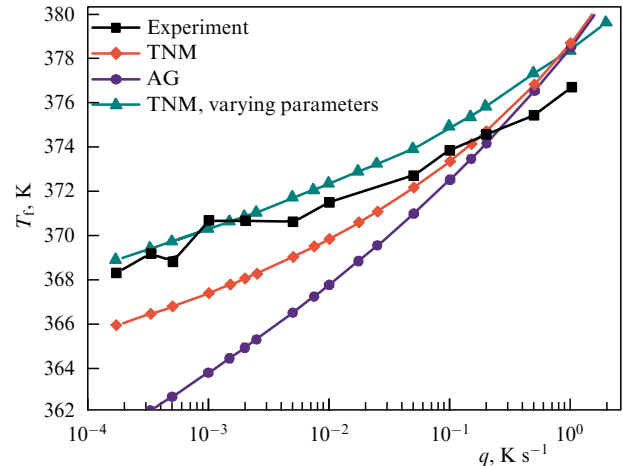


Figure 13. Comparison of the experimental (squares) and calculated values of the limiting fictive temperature. TNM for constant parameters — diamonds; AG for constant parameters — dots; TNM for varying parameters — triangles.

of simulation parameters, the slope of the curve $T_f'(q)$ is substantially different from what is measured, whereas varying two parameters gives a sufficiently good fit. Also note that the model curves intersect the experimental one in the vicinity of $q = 0.5 \text{ K s}^{-1}$, which corresponds to an experiment with equal heating and cooling rates. The implication of this is that the quality of the glass transition kinetics simulation is determined by the heating-to-cooling rate ratio and worsens when this ratio is significantly different from unity [242].

Reference [246] also examined whether the linear extrapolation of the given dependences (Δh and β on q) can be used to predict experimental results. It is shown that the parameters that describe C_p curves best do not correspond to the qualitative description of the dependence of the integral characteristics and the fictive temperature on q .

Presently, similar experimental data are available model simulations are being carried out for polystyrene at large cooling rates (the cooling rate range is $0.1 - 10^4 \text{ K s}^{-1}$, the corresponding heating rate is 5000 K s^{-1}), the modeling of the results is taking place. It is shown that the results of Ref. [246] are clearly manifested for the simultaneous simulation of two sets of data; theoretical methods with a constant set of parameters are unable to describe the observed patterns. It should be noted that other approaches—for example, the configurational entropy hypothesis—run into the same difficulties. For example, in the work carried out in Refs [119, 164] on the polymer glass transition in the range of rates q up to three orders, only the introduction of new phenomenological laws into the dependences of the parameters on the cooling rate was able to improve the agreement between the theoretical and experimental results.

7. Conclusions

Research on and the use of the glass transition long ago entered the sphere of human activity. Studying and optimizing methods for fabricating and processing glass were the preoccupations of people as far back as about five millennia ago. Evidence of interest in glass in ancient civilizations has survived until the present day.

Currently, glass transition kinetics and related processes are one of the central problems in modern condensed matter physics, with original and review papers on the subject numbering in the tens annually. The glass transition process, as noted in the Introduction, is very general in character, similar processes occurring in systems totally different in terms of their properties and the interactions involved. Thus, of extreme interest are spin, structural (covalent, metallic, polymer), dipole, and superconducting glasses. A relatively new class of materials are polymer-based nanocomposite materials [227, 247–249] with various nanoparticle inclusions, among them new promising allotropic carbon forms such as fullerenes and carbon nanotubes [250–254]. The systems listed either are already used in everyday life or hold vast promise for high-technology applications. In this connection, controlling the glass transition process and material properties and predicting the dynamics of property changes under working and extreme temperatures are problems of great importance for practical applications.

Over a few decades, there has been an evolution in describing the glass transition, from simple phenomenological first-order differential equations to modern methods of nonequilibrium thermodynamics and statistical physics. Increasingly, the computer simulation of systems with simple interactions is gaining importance [255–259], which enables the current microscopic theories of the glass transition to be tested. At the same time, as can also be seen from the present review, we are still far from having a complete theory of the glass transition capable of describing the evolution of the full set of properties of a system at temperatures from T_m to T_g (and lower) for an arbitrary experimental thermal history and to fit the wide range of currently available experimental data.

Microscopic approaches and computer simulation deal well with describing certain patterns in the temperature range from the melting point to the glass transition temperature and in some cases are capable of making qualitative predictions. However, close to and within the glass transition range certain corrections should be introduced to such methods as the mode-coupling theory or the random first-order transition theory. Computer simulation does not yet have sufficient computational power to investigate the behavior of systems close to actual ones (at actual cooling rates) in the region of the glass transition, where relaxation lasts for tens or hundreds of seconds. In our view, what the glass transition kinetics of various materials require for its description are approaches based on the thermodynamics of irreversible processes and combined with accurately selected statistical models grounded as far as possible on microscopic considerations. As the glass transition theory develops further, this approach should allow a sufficiently accurate description of experimental data over a wide range of temperatures and of the rates of change of external parameters.

This review presents the state of the art in the study of theoretical approaches to describing glass transition kinetics and physical relaxation. It considers classical theories and a number of present-day methods, analyzes the published studies, and generalizes their results with emphasis on the investigation of the temperature evolution of the heat capacity of polymers in the glass transition interval. This choice, as can be seen, does not narrow the range of applicability of the methods described—indeed, they are adequate for virtually any problem related to the description of the glass transition. Moreover, part of the presented

theories have their origin in other research fields such as spin systems.

The analysis of a wide range of methods and studies which is presented here suggests that at present most calorimetry experiments are described only in the framework of phenomenological approaches such as the Narayanaswamy method or the Adam–Gibbs theory. Furthermore, a detailed description of experiments requires varying model parameters, taking into account their estimates from experiments.

As a promising avenue in the development of theoretical methods in future work, we note the development of microscopic theories of the process and the transition from the description and computer simulation of simple classical experiments to the computer simulation of more complex experiments. Modern theories offer the possibility of the nonempirical description of the general features of the glass transition; in particular, success was achieved in describing the Vogel–Fulcher–Tammann and Kohlrausch laws. The advantages of the modern theories also include the possibility of obtaining predictions by initially specifying the exact expressions for the interaction between the system's particles. Modern computer centers have enough power to perform some calculations in the glass transition temperature range for molecular systems [260] and polymers [261].

With modern experimental techniques, the external parameters and the thermal history characteristics can be varied by more than ten orders of magnitude. For example, in the experiments of Ref. [246], the cooling rate varied by six orders, and adding data from fast calorimetry will extend the range of the parameter q by up to 10 orders. Similarly, studies of the phenomenon of dynamic glass transition [42] allow the frequency of the external influence to be varied over a wide range of 10^{-5} – 10^6 Hz.

However, none of the theoretical approaches listed in this review is yet capable of coping with the problem of the detailed description of experimental data. Another problem that also remains to be solved is the study of the physical relaxation of supercooled systems [65]; at issue here is whether the observed relaxation mechanism is evidence for the bimodal distribution of relaxation times [223] or whether it provides a direct indication of the existence of an ‘intermediate plateau’ in the relaxation process [59]. Solving this and other complex problems requires the development of existing glass transition theories. The possible next step on this path is the development of new physically reasonable expressions for the relaxation time or allowing switching between relaxation mechanisms in a certain temperature range in the glass transition interval or above. It would be a breakthrough if an unequivocal, logically grounded experiment was designed to answer the question of whether the glass transition is a purely kinetic phenomenon or a consequence of the phase transition to the ‘ideal glass’ state.

As regards nonphenomenological theories, such as the mode-coupling theory, these should be developed to describe a great variety of accumulated experimental data. It should be noted that most theoretical studies in this field usually discuss only those experimental data that support the theory or else examine simulation with a simple interaction. Heat capacity curves, for example, do not belong to this category of data, so a necessary step in the development of the theory of the glass transition would be to propose semiempirical expressions capable of describing the $C_p(T)$ dependences at a level not inferior to the existing phenomenological approaches.

Thus, describing the glass transition phenomenon remains a problem of great importance for virtually all fundamental and application fields, and investigations in this area are of extreme interest.

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