

Generalized Vogel Law for Glass-Forming Liquids

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Received April 15, 1988

A model for non-Arrhenius structural and dielectric relaxation in glass-forming materials is based on defect clustering in supercooled liquids. Relaxation in the cold liquid is highly hindered, and assumed to require the presence of a mobile defect to loosen the structure near it. A mild distribution of free-energy barriers impeding defect hopping can generate a wide distribution of waiting times between relaxation events. When the mean waiting time is longer than the time of an experiment, no characteristic time scale exists. This case directly yields the Kohlrausch-Williams-Watts (KWW) relaxation law. A free-energy mismatch between defect and nondefect regions produces a defect-defect attraction, which can lead to aggregation. This may occur in defect-rich "fragile" liquids which also exhibit Vogel kinetics. Defect aggregation and correlation in the "high-temperature" region above the critical consolute temperature T_c is described using the Ornstein-Zernike theory of critical fluctuations. For a defect correlation length divergence $(T - T_c)^{-\nu/2}$, a generalized Vogel law for the structural relaxation time τ results: $\tau = \tau_0 \exp[B/(T - T_c)^{1.5\nu}]$. In the mean-field limit ($\nu = 1$) this provides as good an account of dielectric and structural relaxation in glycerol, *n*-propanol, and *i*-butyl bromide as does the original Vogel law, and for the mixed salt $\text{KNO}_3\text{-Ca}(\text{NO}_3)_2$ and B_2O_3 it also describes kinetics over their entire temperature ranges. A breakdown of the Vogel law in the immediate vicinity of T_g is avoided, and the need to invoke extra low-temperature mechanisms to explain an apparent "return to Arrhenius behavior" is removed.

KEY WORDS: Glass transition; Vogel-Fulcher law; Kohlrausch-Williams/Watts relaxation; Kauzmann paradox.

1. INTRODUCTION

While thermal activation plays a prominent role in all of chemical kinetics, it assumes an especially anomalous form near liquid-to-glass transitions.

This paper is dedicated to Prof. N. G. van Kampen on the occasion of his 67th birthday.

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Here, in the region from 1 to 100 K or more above T_g , the activation energy for structural relaxation becomes temperature dependent, rising sharply as temperature falls, often to values several times larger than the molar heat of vaporization of the liquid. No satisfactory explanation of this behavior has been found, though it is generally recognized that cooperativity is responsible, and the free-volume treatment remains the best "theory."^(1,2)

A second hallmark of the glass transition region, asymmetric Cole–Cole plots with stretched exponential Kohlrausch–Williams–Watts (KWW)^(3,4) correlation functions, has received more attention in recent years, and mechanisms have been found which lead to such distributions.^(5,6) One approach which is readily adopted to polymeric and molecular glasses invokes the idea of defect diffusion (DD).^(5,7) In 1960, in the context of dielectric relaxation, Glarum introduced a model where a frozen-in dipole was relaxed upon its encounter with a mobile defect.⁽⁸⁾ While Glarum considered a single defect and a single dipole in one dimension, in 1975 Bordewijk⁽⁹⁾ generalized this to include a finite concentration of mobile defects in three dimensions. In both cases the mobile defects were undergoing Brownian. Bordewijk's basic result was that, in three dimensions, the dipole–dipole correlation function decays exponentially, which is equivalent to a semicircular Cole–Cole plot. This result seemed to rule out DD mechanisms in viscous disordered materials inasmuch as the latter usually display asymmetric Cole–Cole plots and stretched exponential relaxation. In the next section we review an extended version of the DD model which leads directly to the Kohlrausch law for dielectric decay.^(5,6,10) The relaxation is still assumed to be induced by mobile defects, but the defect motion is characterized by a wide distribution of waiting times rather than by Brownian motion. Then we show how an attraction between defects leads to a condensation of the defect "gas" at T_c below T_g and results in a generalized Vogel law for relaxation rates. Comparison of this generalized Vogel law with experiment indicates improved agreement in cases such as B_2O_3 where data are available quite close to T_g .

2. DEFECT DIFFUSION (DD) AND KOHLRAUSCH RELAXATION^(4–7,10)

2.1. Mobile Defect Formulation

Consider a polarizable material with individual dipole moments $\mu(t)$ in an electric field. When the field is turned off at $t=0$ the decay of the dipole orientation correlation function

$$\phi(t) = \langle \mu(t) \mu(0) \rangle / \langle \mu^2(0) \rangle \quad (1)$$

is related to the frequency-dependent dielectric constant $\varepsilon(\omega)$ of the material by

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_0 - \varepsilon_\infty} = - \int_0^\infty e^{i\omega t} \frac{d\phi(t)}{dt} dt \tag{2}$$

Following Glarum,⁽⁸⁾ we assume that a frozen-in dipole relaxes instantaneously upon its encounter with a mobile defect. Let us start with a system at $t=0$ with one frozen-in dipole and N mobile defects distributed among V lattice sites. For simplicity the V sites are considered to form an perfect 3D lattice and the dipole is placed at the origin of this lattice. Then $\phi(t)$ in Eq. (1) represents the probability that none of the N mobile defects has reached the dipole by time t . It is given by

$$\phi(t) = \left[1 - V^{-1} \sum_{\mathbf{l}_0} \int_0^t F(\mathbf{l}_0, \tau) d\tau \right]^N \tag{3}$$

The term in brackets is one minus the probability that a given defect did reach the origin by time t , i.e., this is the probability that the defect in question did not reach the origin by time t . If the defect started at \mathbf{l}_0 , $F(\mathbf{l}_0, \tau)$ is the probability density that it reached $\mathbf{l}=0$ for the first time at $t=\tau$. This is integrated over all times less than t and averaged over all initial positions of the defect (which has a probability $1/V$ of initially being at a particular lattice site). The bracket is raised to the N th power, as this is the probability that none of the N defects (noninteracting) has yet reached the origin. In the limit $N, V \rightarrow \infty$ with $N/V = c$, a constant concentration of defects, Eq. (3) becomes

$$\phi(t) = \exp \left[-c \sum_{\mathbf{l}_0} \int_0^t F(\mathbf{l}_0, \tau) d\tau \right] \tag{4}$$

which can be shown to be equal to

$$\phi(t) = \exp[-cS(t)] \tag{5}$$

with $S(t)$ the number of distinct lattice sites a defect visits in a time t .

2.2. Distribution of Jump Times

What a defect is and how it moves have not yet been specified. The crux of the physics lies in these issues. We first assume that a defect jumps randomly on the lattice and focus on the kinetics of its hopping. Let $\psi(t)$ be the probability density that a defect remains at a lattice site for a time t . If the defect must jump over an activation barrier of height Δ_0 , then

$$\psi(t) = \lambda_0 \exp(-\lambda_0 t) \tag{6a}$$

with

$$\lambda_0 = v_0 \exp(-\Delta_0/kT) \quad (6b)$$

For a distribution of barrier heights $f(\Delta)$ (but not prefactors) Eq. (6a) is replaced by

$$\psi(t) = \int_0^\infty \lambda e^{-\lambda t} \rho(\lambda) d\lambda \quad (7a)$$

where

$$\rho(\lambda) = f(\Delta) |d\Delta/d\lambda| \quad (7b)$$

The choice

$$\lambda = v \exp(-\Delta/kT) \quad (8a)$$

and

$$f(\Delta) = (kT_0)^{-1} \exp(-\Delta/kT_0) \quad (8b)$$

yields

$$\rho(\lambda) = \frac{1}{\lambda} \left(\frac{\lambda}{v}\right)^\beta \left(\frac{T}{T_0}\right) \quad (8c)$$

which when substituted into Eq. (7a) gives

$$\psi(t) \sim \frac{\beta \Gamma(\beta + 1)}{\lambda_0^\beta} t^{-1-\beta} \quad \text{as } t \rightarrow \infty \quad (9)$$

with $\beta \equiv T/T_0$. The quantity $S(t)$ can be calculated from $\psi(t)$ to give^(5,6)

$$\phi(t) = \exp(-\text{const} \cdot c \cdot t^\beta) \quad (10)$$

where the constant will depend upon β . This expression is valid for $\beta \leq 1$. If $\beta > 1$, exponential decay will result. The complete time dependence of $\phi(t)$, which is somewhat more complicated than Eq. (10), has been given.⁽⁹⁾ Essentially, the decay is initially exponential (due to defects leaving shallow traps) before it crosses over to stretched exponential behavior. The range of validity of Eq. (10) is shown to cover the range of experimental data. Note that to derive Eq. (10), the mean waiting time is $\langle t \rangle \equiv \int_0^\infty t \psi(t) dt = \infty$, i.e., there is no characteristic time scale in the hopping process. The mild distribution of barrier heights induces a wide distribution of hopping times.

If $\langle t \rangle$ were finite, exponential decay, e.g., $\exp(-\text{const} \cdot t/\langle t \rangle)$, would result. The form

$$\phi(t) = \exp(-(t/\tau)^\beta), \quad \beta < 1 \quad (11)$$

is called the Kohlrausch–Williams–Watts (KWW) or stretched exponential law. It was first introduced by Kohlrausch⁽¹¹⁾ in 1854 for the analysis of charge decay in Leyden jars. His son later employed the same model to describe creep in glass and rubber fibers.⁽¹²⁾ Several other examples of creep and stress relaxation were reported,^(13–15) but this law only became widely known after 1970 when Williams and Watts⁽³⁾ discovered its ubiquitous appearance in the dielectric relaxation in polymeric melts near the glass transition. The stretched exponential law has since been found in NMR,⁽¹⁶⁾ remnant magnetization,⁽¹⁷⁾ luminescence studies,⁽¹⁸⁾ optical scattering,⁽¹⁹⁾ and mechanical relaxation.⁽²⁰⁾

Several theories besides defect diffusion, such as hierarchically constrained dynamics and direct transfer, have been proposed to derive the stretched exponential law. The common mathematical basis of these theories is given in ref. 6.

3. DEFECT CLUSTERING AND GENERALIZED VOGEL KINETICS

The model leading to the KWW law of Eq. (11) can be generalized in several ways. First,⁽⁷⁾ one may use activation free energies instead of energies in Eq. (8a). This preserves the KWW form but modifies the linear temperature dependence of β . Second, one can allow the concentration of defects to vary with temperature. For example, if the defects are mobile vacancies which attract each other, as the temperature is lowered they will coalesce into voids (lowering both the energy and entropy). For definiteness, we consider here the case when the defect–defect attraction is strong enough to lead to a condensation of the defect gas (e.g., phase separation from the nondefect component) at a finite temperature T_c below T_g . If the phase transition is second order or weakly first order, the familiar formalism of the 3D lattice gas or Ising model may be used to describe defect concentration fluctuations in the high-temperature pretransition region.⁽²¹⁾ The *net* pair correlation function between defects above T_c will have the Ornstein–Zernike form⁽²²⁾

$$G(r) = \frac{1}{4\pi c R^2} \frac{e^{-\zeta r}}{r} \quad (12)$$

where c is the *total* defect density, R^2 is the second moment of the direct correlation function, and ζ is the reciprocal of the correlation length

between defects. As the temperature falls, the correlation length ζ^{-1} increases in a manner determined by the temperature dependence of the (osmotic) compressibility κ^{-1} . It may be shown that κ and ζ are related by

$$\kappa = A/\zeta^2 \quad (13)$$

At a second-order phase transition κ vanishes⁽²²⁾

$$\kappa = \kappa^0(T - T_c)^\gamma \quad (14)$$

and a Landau or mean-field analysis of the phase transition gives $\gamma = 1$. Combining Eqs. (12)–(14) gives a temperature dependence of the defect correlation length $\zeta^{-1}(T)$,

$$\zeta^{-1}(T) = \zeta_0^{-1}(T - T_c)^{-\gamma/2} \quad (15)$$

and in the mean-field limit (i.e., $\gamma = 1$), Eq. (15) shows that the correlation length between defects diverges as $(T - T_c)^{-\gamma/2}$. As temperature falls, the average size of a cluster grows and the probability of finding an isolated single defect vanishes rapidly. If we assume that *only* isolated defects are mobile enough to bring about dipole relaxation, and that therefore it is the concentration of *isolated defects* which appears as c in Eq. (10), then one may understand non-Arrhenius Vogel behavior as arising from the disappearance of mobile defects through aggregation. To estimate the rate of disappearance of singlets, we write the probability of finding a singlet c_1 as the product of the probability of finding any defect (e.g., c) times the probability that another defect is not correlated with it:

$$c_1 \sim c(1 - c)^z \quad (16)$$

where $1 - c$ is the probability that a neighbor site is not a defect and z is the number of defects "next to" (i.e., correlated with) a given defect. At high temperature where the attraction between defects is low and the correlation length ζ is short, z equals the number of near neighbors, 12 or so. More generally,

$$z = V_{\text{corr}}/V_1 \quad (17)$$

where V_{corr} is the correlation volume around a given defect and V_1 is the volume of a single defect. As temperature falls and the correlation length ζ grows, Eq. (17) becomes

$$z = 1/V_1 \zeta^3 = (T - T_c)^{-1.5\gamma}/V_1 \zeta_0^3 \quad (18)$$

Substituting Eq. (18) into Eq. (16) gives

$$c_1 = c \exp[-B'/(T - T_c)^{1.5\gamma}] \quad (19)$$

where

$$B' = \frac{-\ln(1 - c)}{V_1 \zeta_0^3}$$

When the singlet density of Eq. (19) is combined with Eqs. (10) and (11), the relaxation time is seen to behave as

$$\tau = A \exp[B/(T - T_c)^{1.5\gamma}] \quad (20)$$

where $B \equiv B'/\beta$. Equation (20) is a generalization of the Vogel form:

$$\tau_{\text{Vogel}} = A_v \exp[B_v/(T - T_v)] \quad (21)$$

with the difference that $T - T_c$ appears to the 1.5γ power in Eq. (20). In the next section we apply Eq. (20) (in the mean-field limit $\gamma = 1$) to relaxation data for several glass-forming liquids.

4. APPLICATION OF EQ. (20) TO EXPERIMENT

Figures 1–3 show fits of Eq. (20) to dielectric relaxation data for glycerol, *n*-propanol,⁽²³⁾ and *i*-butyl bromide⁽²⁴⁾ in the temperature range above their glass transitions. As we reported in a preliminary version of this work,⁽¹⁰⁾ Eq. (20) gives a good account of relaxation data, which is also fitted by the Vogel equation, Eq. (21). In such cases the data alone do not provide a means for discriminating between the expressions. Equation (20) is (numerically) “equivalent” to Eq. (21), and the defect model provides an alternative interpretation of the free volume picture.

Figure 4 shows the result of fitting Eq. (20) to viscosity data for the mixed salt $\text{KNO}_3\text{-Ca}(\text{NO}_3)_2$, a case in which it is well known that Eq. (21) breaks down near T_g .⁽²⁵⁾ The fit is excellent over the full range of data available in ref. 25. Similarly, Fig. 5 shows Eq. (20) fitted to viscosity data for B_2O_3 , another example for which the Vogel law breaks down at low temperatures. In fact, the Vogel law overestimates the viscosity at lower temperatures, and it is generally said that a new mechanism sets in, with a return to Arrhenius behavior with a very large exponent.⁽²⁶⁾ It is seen in Figs. 4 and 5 that Eq. (20) fits over the full range of the data, and no evidence of a new mechanism is evident from the data.

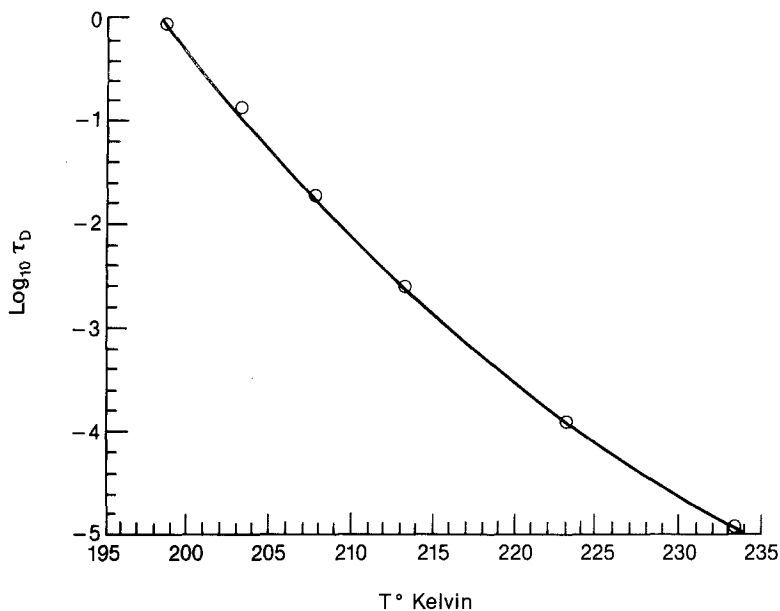


Fig. 1. Temperature variation of dielectric relaxation time in glycerol. Data from ref. 23. Solid line from Eq. (20) with $A = 10^{-12.43}$, $B = 22,719 \text{ K}^{3/2}$, and $T_c = 112.7 \text{ K}$. Parameters for the Vogel equation (21) are given in ref. 20; $A_v = 10^{-14.41}$, $B_v = 2203 \text{ K}$, and $T_v = 132 \text{ K}$. (In ref. 23 there appears to be an error in the value of B . We have adjusted it to fit the data.) The Vogel curve is not shown, since it lies so close to that for Eq. (20). The glycerol T_g is 193 K.

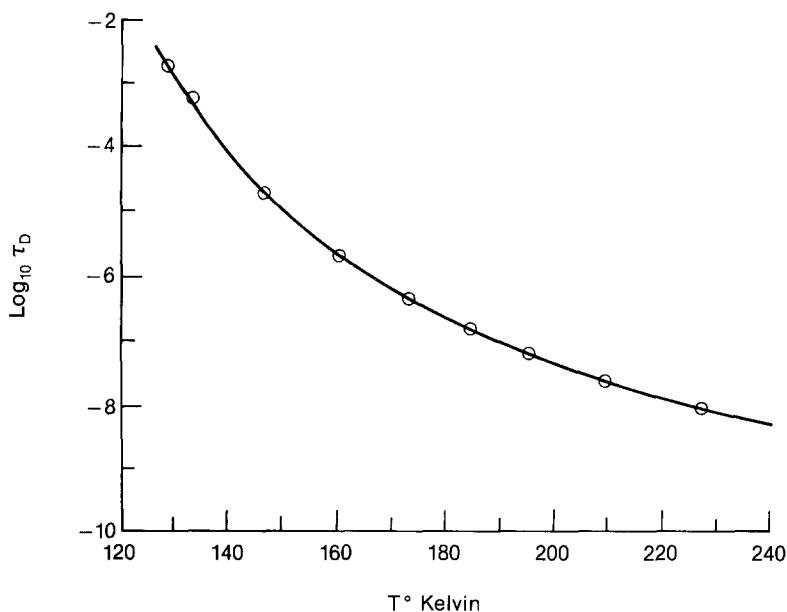


Fig. 2. Temperature variation of dielectric relaxation time in *n*-propanol. Data from ref. 23. Solid line from Eq. (20) with $A = 10^{-10.6}$, $B = 14,964 \text{ K}^{3/2}$, and $T_c = 40.2 \text{ K}$. Parameters for the Vogel equation (21) are given in ref. 20; $A_v = 10^{-10.99}$, $B_v = 1061 \text{ K}$, and $T_v = 73.5 \text{ K}$. The *n*-propanol T_g is 85.2 K.

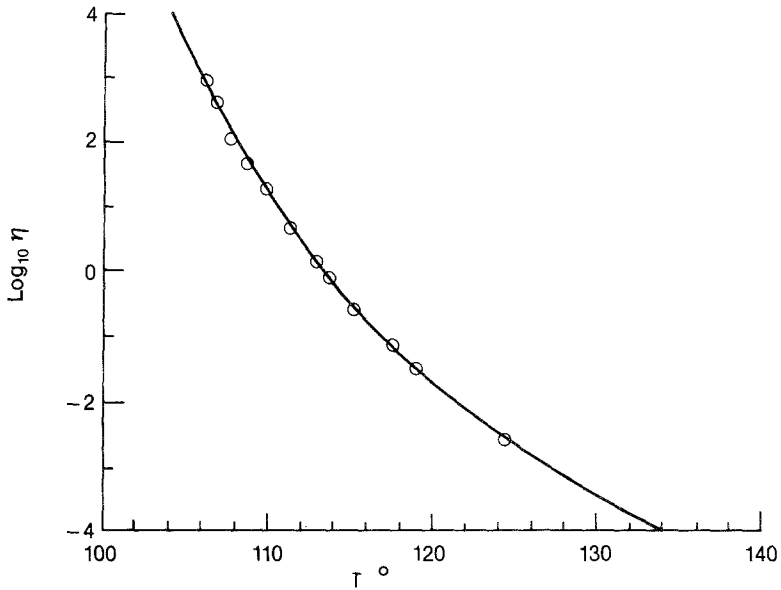


Fig. 3. Temperature variation of viscosity of *i*-butyl bromide. Data from ref. 24. Solid line from Eq. (20) (assuming $\eta = \tau G$, where G is an approximately constant elastic stiffness); with $A = 10^{-8.67}$, $B = 5289 \text{ K}^{3/2}$, and $T_c = 72 \text{ K}$.

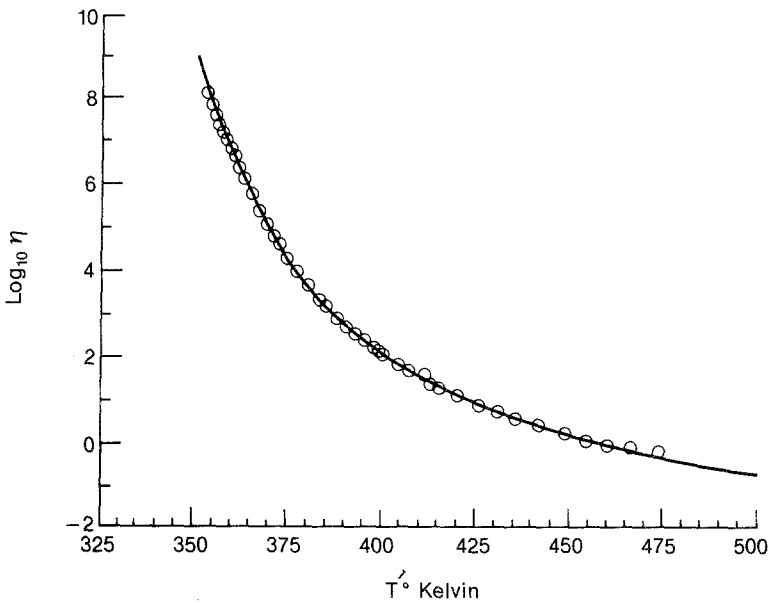


Fig. 4. Temperature variation of viscosity of $\text{KNO}_3\text{-Ca}(\text{NO}_3)_2$. Data from ref. 25. Solid line from Eq. (20) with $A = 10^{-2.55}$, $B = 11,386 \text{ K}^{3/2}$, and $T_c = 292.5 \text{ K}$ ($T_g = 332 \text{ K}$).

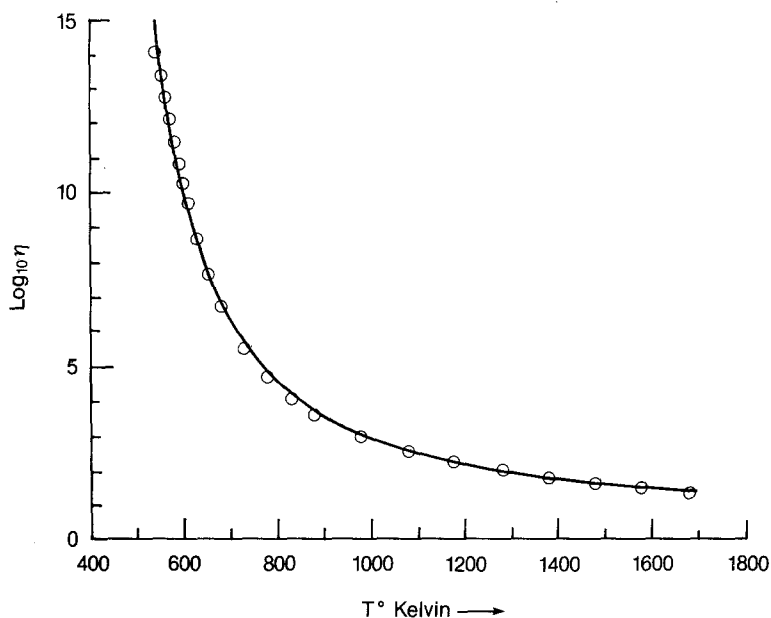


Fig. 5. Temperature variation of viscosity of B_2O_3 . Data from ref. 26. Solid line from Eq. (20) with $A = 10^{0.6029}$, $B = 87,890 \text{ K}^{3/2}$, and $T_c = 337.5 \text{ K}$.

5. DISCUSSION

The defect clustering model of Section 3 assumes that a supercooled liquid is a binary solution of defect and nondefect structures. "Phase separation" should have occurred at the crystallization temperature, with the formation of a translationally and rotationally ordered crystal phase, and simultaneous disappearance and conversion of defect to ordered structures. In complex glass-forming materials, a large nucleation barrier to crystallization permits supercooling of the disordered "mixture," trapping "dissolved" defects and preventing their reorganization and conversion to the lower free-energy structural units. The presence of dissolved defects imparts fluidity to the melt, which is a solid crystal in their absence. The higher free energy of a defect causes a free-energy mismatch with nondefect material, and spatial segregation may occur if this requires a lower activation barrier than conversion of defect to nondefect/crystalline structures. If the free-energy mismatch and defect density are high enough, pretransitional fluctuations and correlations become evident before T_g is reached. The Vogel law T_v of Eq. (21) is interpreted as the temperature at which a binary consolute point would occur if the system mobility (on the time scale of the experiment) did not vanish first.

If the defect density is too low or if the defects are too weakly interacting, Kohlrausch behavior may still be seen [Eq. (11)], but aggregation leading to Vogel-type behavior, Eqs. (20) and (21), will not. This can occur in "strong" liquids (e.g., ref. 27) such as SiO_2 , where defects are highly directional bonding errors which distort the local network and repel other defects from the vicinity. The Kauzmann paradox⁽²⁸⁾ is explained in terms of the underlying phase separation at T_c , since defect aggregation raises the heat capacity and lowers the entropy rapidly in the low-temperature region. A discussion of the thermodynamics of defect aggregation near T_g will be presented elsewhere.

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