

symmetrical dinitrogen tetroxide, ONONO₂, is to some extent chemically analogous to dinitrogen pentoxide, O₂NONO₂. The latter compound can be deposited in covalent form^{27,28} from the vapor phase onto a cold ($T \sim 90^\circ\text{K}$) window. It is transformed to the ionic form upon warming to 195°K.^{27,28} Also, in highly polar solvents it exists in the ionic form.

The discussion of the chemical mechanism of formation of nitrosonium nitrate will be presented elsewhere

²⁷ R. Teranishi and J. C. Decius, *J. Chem. Phys.* **22**, 896 (1954).

²⁸ I. C. Hisatsune, J. P. Devlin, and Y. Wada, *Spectrochim. Acta* **18**, 1641 (1962).

in conjunction with the results of previous preparatory work.⁴ Nitrosonium nitrate is a very reactive compound. It undergoes electrophilic addition reactions to some olefins at cryogenic temperatures. The details of this work will be the subject of a forthcoming publication.

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On the Temperature Dependence of Cooperative Relaxation Properties in Glass-Forming Liquids*

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A molecular-kinetic theory, which explains the temperature dependence of relaxation behavior in glass-forming liquids in terms of the temperature variation of the size of the cooperatively rearranging region, is presented. The size of this cooperatively rearranging region is shown to be determined by configuration restrictions in these glass-forming liquids and is expressed in terms of their configurational entropy. The result of the theory is a relation practically coinciding with the empirical WLF equation. Application of the theory to viscosimetric experiments permits evaluation of the ratio of the kinetic glass temperature T_g (derived from usual "quasistatic" experiments) to the equilibrium second-order transition temperature T_2 (indicated by either statistical-mechanical theory or extrapolations of experimental data) as well as the hindrance-free energy per molecule. These parameters have been evaluated for fifteen substances, the experimental data for which were available. Hindrance-free energies were found to be of the magnitude to be expected from consideration of molecular interaction energies. The values of T_g/T_2 thus obtained for these fifteen widely differing materials were found to be nearly the same, i.e., $1.30 \pm 8.4\%$. Values for T_g/T_2 of nearly the same magnitude were derived by Bestul and Chang from calorimetric data.

INTRODUCTION

THE temperature dependence of dynamic-mechanical or dielectric relaxation behavior in supercooled liquids near the glass temperature shows marked departure from a simple Arrhenius behavior with a temperature-independent activation energy.

An empirical relation describing this temperature dependence has been given by Williams, Landel, and Ferry.¹⁻³ This WLF equation, as it is often called, has

the following form:

$$-\log a_T = C_1(T - T_s) / [C_2 + (T - T_s)]. \quad (1)$$

Here $a_T = \tau(T) / \tau(T_s)$ is the ratio of relaxation times at temperatures T and T_s , respectively.

These authors showed that the values $C_1 = 8.86^\circ$ and $C_2 = 101.6^\circ\text{C}$ provide a good fit to the experimental data for a relatively large number of substances, provided the parameter T_s is chosen appropriately for each.

The validity of an equation of the same form as (1) with another choice, T'_s , for the reference temperature and new values, C'_1 and C'_2 , for the coefficients in the equation can then be demonstrated by observing that

$$\begin{aligned} -\log a_{T'} &= -\log \frac{\tau(T)}{\tau(T'_s)} = -\log \frac{\tau(T)}{\tau(T_s)} + \log \frac{\tau(T_s)}{\tau(T'_s)} \\ &= -\log a_T + \log a_{T'_s} \end{aligned} \quad (2)$$

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¹ M. L. Williams, *J. Phys. Chem.* **59**, 95 (1955).

² M. L. Williams, R. F. Landel, and J. D. Ferry, *J. Am. Chem. Soc.* **77**, 3701 (1955).

³ An equation, $\ln \tau = A' + B / (T - T_\infty)$, which leads to the WLF equation was introduced earlier by H. Vogel, *Physik. Z.* **22**, 645 (1921), and used by G. Tammann and G. Hesse, *Z. Anorg. Allgem. Chem.* **156**, 245 (1926), for the interpretation of viscosimetric measurements and by D. Davidson and R. H. Cole, *J. Chem. Phys.* **19**, 1484 (1951), for the interpretation of dielectric measurements on supercooled liquids.

and using Eq. (1) for $\log a_T$ and $\log a_{T_s}$. C_1' and C_2' prove to be given by the formulas⁴

$$C_1' = C_1 C_2 / [C_2 - (T_s - T_s')], \quad (3)$$

$$C_2' = C_2 - (T_s - T_s'). \quad (4)$$

Williams, Landel, and Ferry² observed, furthermore, that for many materials that value T_s which yields the particular "semiuniversal" values $C_1 = 8.86$ and $C_2 = 101.6^\circ\text{C}$ is located roughly 50°C above the glass temperature T_g , determined as the temperature where a break occurs in the volume-vs-temperature plot of "quasistatic" volume-expansion measurements. To the extent that this is true, it is also true [as can be seen from Eqs. (3) and (4)] that other "semiuniversal" WLF constants, C_1' and C_2' , correspond to other roughly constant values of the difference, $T_s' - T_g$, between reference temperature and glass temperature for various materials. In particular the choice $T_s' - T_g = 0$ gives

$$-\log a_T = 17.44(T - T_g) / [51.6 + (T - T_g)], \quad (5)$$

which is more usually referred to as the WLF equation. Thus, if for all substances $T_s - T_g$ were exactly equal to 50°C , Eq. (5) would be a universal relation describing the variation with temperature of the relaxation behavior of all glass-forming liquids.

In spite of the appreciable departures of many materials from the relation $T_s - T_g = 50^\circ\text{C}$, much effort has been expended to explain the "universal" Eq. (5) by free-volume concepts.^{2,4-8} However, a departure of as little as 5 to 10°C , as is frequently found, from the presupposed relation $T_s - T_g = 50^\circ\text{C}$ implies large deviations from the "universal" values $C_1' = 17.44^\circ$ and $C_2' = 51.6^\circ\text{C}$ to fit the experimental data. So the "universality" of Eq. (5) seems quite poor insofar as quantitative description is attempted.

Furthermore, the "free volume" is ill defined operationally. Especially in the case of polymers to which most of the data refer, the "free volume" cannot be associated with a real molecular volume but has to be interpreted in a hitherto undefined way on the basis of inter- and intramolecular interaction, as well as the topology of molecular packing in the amorphous phase.

The principal aim of the present investigation, therefore, is to relate by statistical-mechanical argument the relaxation properties of glass-forming liquids to their "quasistatic" properties, characterized by, for example, the glass temperature and the specific heats of the glass and the equilibrium melt.

The "quasistatic" glass temperature T_g is, of course, understood to be the temperature below which molecular relaxation times are too long to permit establish-

ment of equilibrium in the duration of even the slowest experiments ("time scale" of hours to days).

It is also understood now⁹ that this great increase in relaxation times attendant upon cooling a system in the neighborhood of this glass temperature is associated with the decrease to very small values in the number of configurations available to the system in this region. This dearth of configurations is manifest in the smallness of the equilibrium entropy near the glass temperature. Kauzmann noted,¹⁰ in fact, that extrapolations of plots of equilibrium data, obtained above the glass temperature, to temperatures below the glass temperature yielded various thermodynamic "catastrophes" such as negative configurational entropies. It was later recognized that, among these catastrophes, the entropy catastrophe was the fundamental paradox requiring resolution, since it was always encountered first on following these extrapolations to lower temperatures. Furthermore, the temperature at which it occurs seems always to be about 50°C below the glass temperature. In this connection, it is of paramount interest that the WLF equation yields infinite relaxation times about 50°C (actually 51.6°C) below the glass temperature.

The statistico-mechanical quasilattice theory of Gibbs and DiMarzio⁹ gave this decrease in entropy to small values and resolved the paradox of negative configurational entropies at lower temperatures through demonstration of a second-order transition at the temperature T_2 where the configurational entropy vanishes. Below T_2 the configurational entropy remains, of course, zero, rather than going to meaningless negative values. More remarkable was the result that the variation in the theoretically predicted T_2 with such quantities as molecular weight, percent of monomer as plasticizer, composition in the case of copolymers, degree of cross linking, etc., correlated almost perfectly with the corresponding experimentally observed variations in T_g . The existence of an unknown parameter ("chain-stiffness energy") in the theory prevented the determination of the absolute value of the difference $T_g - T_2$ (or ratio T_g/T_2) though not the demonstration of its approximate constancy with variations in the aforementioned quantities.

The inescapable conclusion of these observations was the one mentioned above, namely that the sluggish relaxation behavior governing T_g is itself a manifestation of the smallness of the entropy (dearth of configurations) in the region immediately above T_2 . This qualitative conclusion concerning the relaxation phenomena, which could be obtained from the comparison of the quantitative theory for the equilibrium properties with experimental data, could not, however, yield the

⁴ J. D. Ferry, *Viscoelastic Properties of Polymers* (John Wiley & Sons, Inc., New York, 1961), Chap. 11.

⁵ F. Bueche, *J. Chem. Phys.* **21**, 1850 (1953); **24**, 418 (1956); **30**, 748 (1959).

⁶ M. H. Cohen and D. Turnbull, *J. Chem. Phys.* **31**, 1164 (1959).

⁷ A. J. Kovacs, *Compt. Rend.* **250**, 109 (1960).

⁸ J. D. Ferry and R. A. Stratton, *Kolloid-Z.* **171**, 107 (1960).

⁹ J. H. Gibbs and E. A. DiMarzio, *J. Chem. Phys.* **28**, 373 (1958); **28**, 807 (1958); *J. Polymer Sci.* **40**, 121 (1959); *ibid.*, **A1**, 1417 (1963); J. H. Gibbs, *Modern Aspects of the Vitreous State* (Butterworths Scientific Publications, Ltd., London, 1960) Chap. 7.

¹⁰ W. Kauzmann, *Chem. Rev.* **43**, 219 (1948).

quantitative relation between T_g and T_2 . The determination of this quantitative relation between T_g and T_2 is, then, another aim of the quantitative nonequilibrium theory presented in this paper.

We note that in contradistinction to T_g , which is not a particularly fundamental quantity (varying as it does with varying experimental time scales¹¹), the value of T_2 is a rather profound measure of various properties of a substance. Thus, we may anticipate from the foregoing discussion that, whereas the choice of T_g as the reference temperature in a WLF-type equation may be useful, the appearance of T_2 in a theoretically derived version of a WLF-type equation should be inescapable and of fundamental significance.

Thus the aim, stated above, to relate relaxation properties to such quasistatic properties as T_g , etc., is seen to be equivalent to the aim to relate these relaxation properties to such, more fundamental, thermodynamic properties as T_2 .

The transition probabilities for the liquid will be formulated in terms of the equilibrium distribution of an isothermal-isobaric ensemble of small systems of the size of the cooperatively rearranging region.¹² The essential step will prove to be the evaluation of the temperature dependence of the size of this "cooperatively rearranging" region, defined as the smallest region that can undergo a transition to a new configuration without a requisite simultaneous configurational change on and outside its boundary.

At T_2 the cooperatively rearranging region must, of course, comprise the whole sample (or macroscopic parts of it) since, at this temperature, there is only one (or very few) available configuration(s) for even the whole system (configurational entropy zero). At higher temperatures, however, the much larger number of configurations available to the system allows individual rearrangements into different configurations for microscopic cooperative regions.

In the treatment presented here only the most general thermodynamic results of the theory of Gibbs and DiMarzio⁹ will be needed. A more detailed calculation, using explicitly the lattice model of polymer phases to

¹¹ A. J. Kovacs, *Fortschr. Hochpolymer. Forsch.* **3**, 394 (1963).

¹² The concept of a temperature dependence of the size of the cooperatively rearranging region was, to our knowledge, first introduced by E. Jenckel, *Z. Physik. Chem.* **184**, 309 (1939). Jenckel, however, formulated this temperature variation in terms of the energy of packing ("Käfigeffekt"), whereas our treatment emphasizes the decisive role of the entropy of molecular packing. R. M. Barrer, *Trans. Faraday Soc.* **38**, 322 (1942); **39**, 48, 59 (1943), based the molecular-kinetic theory of transport processes in liquids on the theory of the kinetics of unimolecular reactions. He connected the observed temperature variation of the energy of activation with "loosening or breakdown of complex structures on activation."

A specification of the cooperative region in glass-forming liquids, similar to that used in the present treatment, was given by one of the authors in a theoretical description of volume and enthalpy relaxation processes in organic glasses, G. Adam, *Kolloid-Z.* **180**, 11 (1962); **195**, 1 (1964). In accordance with the small temperature range of the corresponding experiments, however, the size of the cooperative region was approximated as temperature independent.

derive the transition probabilities will be published separately.¹³

PROBABILITIES OF COOPERATIVE REARRANGEMENTS

The temperature-dependent relaxation times in dynamic-mechanical or dielectric experiments in liquids are determined by the probabilities of cooperative rearrangements.

To evaluate these transition probabilities, we define a cooperatively rearranging region as a subsystem of the sample which, upon a sufficient fluctuation in energy (or, more correctly, enthalpy), can rearrange into another configuration independently of its environment.

The number of molecules (or monomeric segments in the case of polymers) in such a cooperative region will be denoted by z .

Our treatment considers the probability of a cooperative rearrangement in a fixed subsystem as a function of its size z . If one were to consider different possible choices for a (spherical) cooperative region surrounding a representative molecule, this would introduce, into a pre-exponential factor, only a factor proportional to z , whose temperature dependence is negligible to that of the exponential function of z that arises [see Eq. (8)].

We may assume that the subsystem of z molecules interacts only weakly with the macroscopic system. Since the subsystems are in both mechanical and thermal contact with each other, we consider an isobaric-isothermal ensemble of N independent, equivalent, and distinguishable subsystems composed of a z molecular segments each. In describing the probability of the relevant fluctuations we may consider the distribution of the subsystems of the ensemble to depart negligibly from an equilibrium distribution.

Now we sort the subsystems into two classes, those, n in number, that reside in states which allow a cooperative rearrangement and the $N-n$ that are in states not allowing a transition.

The isothermal-isobaric partition function for the ensemble is given by

$$\Delta(z, P, T) = \sum_{E, V} w(z, E, V) \exp(-E/kT) \exp(-PV/kT), \quad (6)$$

where w is the degeneracy of energy-level E and volume V of the subsystem. The Gibbs free energy is, of course, given by $G = z\mu = -kT \ln \Delta$.

If we sum over only the values of E and V that permit a transition, we get a "partition function" $\Delta'(z, P, T)$ and corresponding "Gibbs free energy" $G' = z\mu' = -kT \ln \Delta'$ for the rearrangeable subsystems.

Now among all subsystems the fraction that is in states permitting rearrangements (transitions) is given by

$$n/N = \Delta'/\Delta = \exp[-(G' - G)/kT]. \quad (7)$$

¹³ G. Adam and J. H. Gibbs (to be published).

The cooperative transition probability $W(T)$ is proportional to n/N . Thus, using the notation $z\Delta\mu = z(\mu' - \mu) = G' - G$, we have

$$W(T) = A \exp(-z\Delta\mu/kT). \quad (8)$$

This equation represents the transition probability of a cooperative region as a function of its size z .

The frequency factor A can be assumed negligibly dependent on temperature and z in comparison to the exponential function and, therefore, need not be evaluated more closely for our present purposes.

Physically, $\Delta\mu$ is largely the potential energy hindering the cooperative rearrangement per monomer segment. As suggested by the detailed treatment of the molecular model,¹³ in a good approximation the dependence of $\Delta\mu$ on T and z can be neglected.

To arrive at the average transition probability $\bar{W}(T)$, we have to sum over all possible, i.e., nonvanishing, values of $W(T)$, corresponding to different z .

As is shown in the next section, there is a critical lower limit z^* to the sizes of cooperative regions that can yield nonzero transition probabilities.

Thus, we have for the average transition probability

$$\bar{W}(T) = \sum_{z=z^*}^{\infty} A \left[\exp\left(\frac{-\Delta\mu}{kT}\right) \right]^z. \quad (9)$$

The summation of this truncated geometrical progression gives

$$\bar{W}(T) = \frac{A}{1 - \exp(-\Delta\mu/kT)} \exp\left(\frac{-z^*\Delta\mu}{kT}\right). \quad (10)$$

The denominator $[1 - \exp(-\Delta\mu/kT)]$ is nearly equal to unity and, therefore, negligibly dependent on temperature in comparison with the numerator. We may, therefore, absorb this factor into a new frequency factor \bar{A} , approximately independent of temperature, obtaining instead of Eq. (10)

$$\bar{W}(T) = \bar{A} \exp(-z^*\Delta\mu/kT). \quad (11)$$

This result states simply that the overwhelming majority of transitions are undergone by regions whose size differs negligibly from the smallest size z^* that permits a transition at all. It is an expression of the fact that the transitions of these smallest cooperative regions involve the smallest number z^* of monomer units surmounting, essentially simultaneously, the individual barriers restricting their arrangement.

Thus, we are left with the task of evaluating the temperature dependence of this critical size, z^* .

CRITICAL SIZE OF THE COOPERATIVE REGION

We assume that it is possible to factor from the (complete) partition function Δ of our isothermal-isobaric ensemble of subsystems the configurational partition function Δ_c corresponding to the potential energy part E_{pot} of the Hamiltonian function of the subsystem. This configurational partition function can be

written

$$\Delta_c(z, P, T) = \sum_{E_{\text{pot}}, V} w_c(z, E_{\text{pot}}, V) \times \exp(-E_{\text{pot}}/kT) \exp(-pV/kT), \quad (12)$$

where w_c is the number of configurations of a subsystem in a state characterized by E_{pot} and V .

Thus, the configurational entropy of a subsystem is defined by

$$s_c = -(\partial G_c / \partial T)_{p, z}, \quad (13)$$

where

$$G_c = -kT \ln \Delta_c. \quad (14)$$

The configurational entropy S_c of the macroscopic supersystem can be defined in the same way. In the macroscopic limit, however, the configurational entropy can be expressed directly as the logarithm of the number of configurations W_c of the maximal term of the partition function, i.e., the term corresponding to the average potential energy U and the average volume \mathcal{V} of the system,

$$S_c = k \ln W_c(U, \mathcal{V}). \quad (15)$$

On the other hand, using the assumption of equivalence and independence of the subsystems and Eqs. (12) and (13), one can show the following.¹⁴ The configurational entropy S_c of a macroscopic supersystem composed of N subsystems is generally given by

$$S_c = N s_c, \quad (16)$$

where s_c again is the configurational entropy of a subsystem of z monomer units.

Thus, we may express the configurational entropy of a cooperative subsystem as the logarithm of an average number $W_c^{1/N}$ of configurations

$$s_c = k \ln(W_c^{1/N}). \quad (17)$$

This average number of configurations of a subsystem depends, of course, on z , the size of the subsystem. If we consider the macroscopic system to consist of just a mole of segments we have

$$s_c = k \ln(W_c^{z/N_A}), \quad (18)$$

where N_A is Avogadro's number. This equation shows explicitly that for a given temperature and pressure (i.e., given W_c) the configurational entropy of a subsystem increases monotonically with the size of the subsystem, as it should.

Now there must be a lower limit z^* to the size of a cooperative subsystem that can perform a rearrangement into another configuration, this lower limit corresponding to a critical average number $W_c^{z^*/N}$ of configurations available to the subsystem. Certainly, this smallest size must be sufficiently large to have at least two configurations available to it, one in which the region resides before the transition and another into

¹⁴ See for instance: T. L. Hill, J. Chem. Phys. **36**, 3182 (1962).

which it may move. Thus, the lower limit z^* of the size of the representative cooperatively rearranging region may be characterized by a critical configurational entropy s_c^* given by

$$s_c^* = k \ln(W_c^{z^*/NA}). \quad (19)$$

For the following, however, we need not specify the numerical value of this small critical entropy s_c^* .

Thus, we finally can express the critical size z^* of the cooperative region in terms of the molar configurational entropy S_c of the macroscopic sample as

$$z^* = N_A s_c^* / S_c. \quad (20)$$

Inserting this equation into the expression for the average transition probability, Eq. (11), yields¹⁵

$$\bar{W}(T) = \bar{A} \exp(-\Delta\mu s_c^*/kT S_c) = \bar{A} \exp(-C/T S_c). \quad (21)$$

This equation exhibits explicitly the dependence of the transition probability on the configurational entropy of the glass-forming liquid.^{15a} Its derivation is based essentially on the assumption of independent and equivalent subsystems, i.e., on the premise of weak interaction of a cooperative region with its environment.

TEMPERATURE SHIFT FACTOR

Since the relaxation time is reciprocally related to the transition probability

$$\tau(T) \propto 1/\bar{W}(T), \quad (22)$$

the logarithmic shift factor can be written

$$\log a_T = \log[W(T_s)/W(T)]. \quad (23)$$

Using Eq. (21), we get

$$-\log a_T = 2.303 \left(\frac{\Delta\mu s_c^*}{k} \right) \left[\frac{1}{T_s S_c(T_s)} - \frac{1}{T S_c(T)} \right]. \quad (24)$$

To evaluate the temperature dependence of $S_c(T)$, we observe that the specific heat of glass-forming liquids is approximately independent of temperature. From

$$S_{cb} - S_{ca} = \int_{T_a}^{T_b} \left(\frac{\Delta C_P}{T} \right) dT, \quad (25)$$

we have in this approximation

$$S_c(T) - S_c(T_s) = \Delta C_P \ln T/T_s, \quad (26)$$

and, using $S_c(T_2) = 0$,

$$S_c(T_s) = \Delta C_P \ln T_s/T_2. \quad (27)$$

¹⁵ Here and later, the hindrance-free enthalpy $\Delta\mu$ is taken per mole.

^{15a} Note added in proof: M. Goldstein has pointed out (private communication) that the appearance of $T S$, rather than S alone, in a basic relaxation equation would circumvent his objection [J. Chem. Phys. **39**, 3369 (1963)] to emphasis on the entropy (in Ref. 9) as the principal variable governing glass formation. See Eq. (21) of this article.

Here ΔC_P is the difference in specific heat between the equilibrium melt and the glass at T_g .

Introducing Eqs. (26) and (27) into Eq. (24) and rearranging the resulting formula algebraically yields without further approximations

$$-\log a_T = a_1(T - T_s) / [a_2 + (T - T_s)], \quad (28)$$

where

$$a_1 = 2.303 \frac{C}{\Delta C_P T_s \ln(T_s/T_2)} \quad (29)$$

and

$$a_2(T) = \frac{T_s \ln(T_s/T_2)}{\ln(T_s/T_2) + [1 + T_s/(T - T_s)] \ln T/T_s}. \quad (30)$$

For numerical inspection it is convenient to develop $\ln T/T_s$ in the denominator of Eq. (30)

$$a_2(T) = T_s \ln\left(\frac{T_s}{T_2}\right) / \left[1 + \ln\left(\frac{T_s}{T_2}\right) + \sum_{i=1}^{\infty} \frac{(-1)^{i-1}}{i(i+1)} \left(\frac{T - T_s}{T_s}\right)^i \right]. \quad (31)$$

Thus, the result of the kinetic theory is a formula of the WLF type, where the parameters are not necessarily universal and one of them (a_2) is slightly temperature dependent.

Since both parameters, a_1 and a_2 , depend on T_s/T_2 , comparisons of Eqs. (28)–(30), for a given T_s , with experimental data for a given substance should give the value of the equilibrium second-order transition temperature T_2 for that substance. Such results are presented in a later section.

CONCERNING "UNIVERSALITY" OF THE WLF PARAMETERS

We have cited, in the Introduction, the evidence of Williams, stating that the relaxation behavior of glass-forming substances can often be described by Eq. (1) with the "universal" parameters $C_1 = 8.86$ and $C_2 = 101.6^\circ\text{C}$, provided T_s is appropriately chosen. We must now determine the conditions under which Eqs. (29) and (30) will yield such "universal" parameters.

Without abbreviations Eq. (29) states that

$$a_1 = 2.303 \Delta\mu s_c^* / k \Delta C_P T_s \ln(T_s/T_2). \quad (29')$$

Since $a_2(T)$ is practically equal to $a_2(T_s)$, Eq. (30) implies that

$$a_2 = \frac{T_s \ln(T_s/T_2)}{1 + \ln(T_s/T_2)}. \quad (30')$$

Strictly speaking, then, the ratio $\Delta\mu s_c^* / \Delta C_P$ would have to be nearly the same among all the members of a set of substances if their values of a_1 and a_2 were to be identical. On the other hand, since $\ln T_s/T_2 \ll 1$, it is essentially the quantity $T_s \ln T_s/T_2$ which, according to Eqs. (29') and (30') for given $\Delta\mu s_c^* / \Delta C_P$, governs

TABLE I. Properties of glass-forming liquids. Explanations are given in the text.

	T_g (°K)	T_g' (°K)	C_2' (°C)	C_1'	T_g/T_2	T_2 (°K)	$T_g - T_2$ (°C)	ΔC_P (cal mole ⁻¹ ·deg ⁻¹)	$\Delta\mu_{s_c}^*/k$ (kcal mole ⁻¹)
Polyisobutylene	243	202	60.6	14.85	1.53	132	70	5.33 ^a	2.69
Polystyrene	418	373	56.6	15.90	1.20	311	62	6.45 ^b	3.02
Polyvinyl acetate	351	305	55.6	16.20	1.25	244	61	12.40 ^c	5.95
Polyvinyl chloroacetate	346	296	51.6	17.44	1.23	240	56
Polymethyl acrylate	324	276	53.6	16.80	1.27	217	59
Polymethyl methacrylate	435	378	44.6	20.20	1.14	332	46	6.30 ^d	2.74
Polyvinyl chloride	396	347	52.6	17.15	1.20	289	58	4.37 ^a	2.05
Polyurethan	283	238	56.6	15.90	1.27	187	51
75/25 Butadiene-styrene copolymer	268	211	44.6	20.20	1.31	161	50	6.95 ^a	3.47
Hevea rubber unvulcanized	251	200	50.6	17.80	1.40	143	57	6.66 ^a	3.47
Glucose	351	305	57.6	15.65	1.26	242	63	32.75 ^a	15.6
<i>n</i> -Propanol	143	(98)	56.6	15.90	(3.93)	(25)	(73)	(9.62) ^a	(8.93)
Propylene glycol	217	160	42.6	21.13	1.43	112	48	16.1 ^a	8.43
Glycerol	238	187	50.6	17.8	1.45	129	58	19.5 ^a	10.5
Cellulose tributyrate in dimethyl phthalate 21%	247	188	42.6	21.13	1.34	140	48
Cellulose tributyrate in dimethyl phthalate 43%	256	193	38.6	23.30	1.28	151	42

^a B. Wunderlich, J. Phys. Chem. **64**, 1052 (1960).

^b K. Überreiter and E. Otto Laupenmühlen, Z. Naturforsch. **8a**, 664 (1953).

^c M. V. Volkenstein and Y. Y. Sharonov, Vysokomolekul. Soedin. **4**, 917 (1962).

^d A. J. Kovacs, Fortsch. Hochpolymer. Forsch. **3**, 394 (1963).

the magnitude of a_1 and a_2 , i.e., of C_1 and C_2 . Thus, the variation of T_2 for different materials can easily be compensated by a proper choice of $T_s \ln T_g/T_2$, i.e., of T_s .

This means that the validity of the Williams parameters $C_1=8.86$ and $C_2=101.6^\circ\text{C}$ for different glass-forming materials rests essentially on the constancy of the values of $\Delta\mu_{s_c}^*/\Delta C_P$ among these substances. Such approximate constancy of $\Delta\mu_{s_c}^*/\Delta C_P$ can be understood at least qualitatively from a molecular point of view. The quantity s_c^* represents the general topological condition for a cooperative transition to be possible and should be nearly the same for all glass-forming liquids. The quantity $\Delta\mu$ is essentially the height of the potential-energy barrier per monomer unit, whereas ΔC_P is proportional to the differences between the minima of the potential-energy curve. Evidently, in cases involving strong molecular interactions, i.e., hydrogen-bonding substances, both $\Delta\mu$ and ΔC_P should have greater values than in cases involving only weak van der Waals interactions. The ratio $\Delta\mu/\Delta C_P$ might well be of a similar magnitude in both cases.

However, an exact constancy of $\Delta\mu_{s_c}^*/\Delta C_P$ for different substances seems not to be required, either by the molecular theory or by the experimental data. The

experimental shift factors which are described by Eq. (1) with "universal" values C_1 and C_2 extend only over a restricted range of temperature, usually much less than 100°C , and this range never includes the critical region between T_g and T_2 . On the other hand, the WLF function is one of monotonically varying slope and curvature. Thus, particularly in view of the experimental errors, one has the possibility, only by adjusting T_s , of forcing Eq. (1) with "wrong but universal" values of C_1 and C_2 , to fit the experimental data for many substances of varying $\Delta\mu_{s_c}^*/\Delta C_P$.

COMPARISON WITH EXPERIMENTS

For the comparison of the kinetic theory with experimental data we use the WLF Eq. (1) with the parameters $C_1=8.86$ and $C_2=101.6^\circ\text{C}$ and T_s adjustable as a convenient means of displaying these experimental data. The WLF equation with these values of the parameters C_1 and C_2 describes the temperature dependence of the shift factor, $\ln a_T$, for ~ 20 different glass-forming liquids over a temperature range of 100°C within the experimental errors, provided the reference temperature is properly chosen.^{1,2,4} We use the compilation of data given by Ferry⁴ in his Table 11-III. In our Table I are reproduced his values for T_g and T_g' . From $T_g - T_g'$ we can calculate, from Eqs. (3) and

(4), values of C_1' and C_2' appropriate to use of T_g as a reference temperature for the shift factor. The values of C_1' and C_2' , thus derived, are given in Table I. They are no longer universal but represent the experimental data using T_g as a reference temperature.

We must now compare these "experimental" values with the theoretical expressions (29) and (30) with T_g chosen for T_s . The comparison of C_2' with $a_2(T_g)$ given by Eq. (30') gives the following relation for the determination of the ratio T_g/T_2

$$T_g/T_2 = \exp[(T_g/C_2') - 1]^{-1}. \quad (32)$$

The values T_g/T_2 , T_2 and $T_g - T_2$, determined by Eq. (32), are given in Table I.

With the exception of *n*-propanol, the factor T_g/T_2 shows a remarkable constancy for all the widely differing materials. In the case of *n*-propanol the experimental figures are not known very precisely because the measurements did not cover the entire glass-transformation region and yield the value of T_g .¹⁶ Excluding *n*-propanol, we determine from Table I the following mean values for T_g/T_2 and $T_g - T_2$, as well as their average deviation from the mean value:

$$T_g/T_2 = 1.30 \pm 8.4\%, \\ T_g - T_2 = 55^\circ\text{C} \pm 10.9\%.$$

Although the precise figures are not very significant, as can be inferred from both the discussion at the end of the foregoing section and an awareness of the approximations in our theoretical derivation, the correlation between T_g and T_2 indicates that the configurational entropy of the melt indeed determines the temperature dependence of cooperative relaxation processes in the glass-transition region.

Values of T_g/T_2 similar in magnitude to those in Table I were derived by an empirical "free-entropy" interpretation of the experimental data by Bestul and Chang.¹⁷

The comparison of C_1 with a_1 yields the following relation for $\Delta\mu s_c^*/k$

$$\Delta\mu s_c^*/k = C_1' T_g \Delta C_P(T_g) \log T_g/T_2. \quad (33)$$

We have included in Table I the available values of $\Delta C_P(T_g)$ from calorimetric measurements. The corre-

¹⁶ An alternate approach, avoiding the poorly known glass temperature of *n*-propanol as a reference temperature in the WLF equation, is to use the original data of Tammann and Hesse and of Davidson and Cole.³ These experimental results were represented by $\ln\tau = A' + 460/(T - 73.5)$ with T expressed in $^\circ\text{K}$. From Eqs. (21), (23), (26), and (27), using the approximation $[(T - T_2)/T_2]^2 \ll 1$, one can derive $\ln\tau = \text{const.} + \Delta\mu s_c^*/k \Delta C_P(T - T_2)$. The comparison with the empirical equation yields immediately $T_2 = 73.5^\circ\text{K}$ and $\Delta\mu s_c^*/k \Delta C_P = 460^\circ\text{C}$.

With $80^\circ\text{K} < T_g < 100^\circ\text{K}$, we have $1.09 < T_g/T_2 < 1.36$, a range which compares well with the figures T_g/T_2 for other compounds given in Table I.

Using $\Delta C_P = 9.62 \text{ cal mole}^{-1} \text{ deg}^{-1}$ (see Table I) and $s_c^* = k \ln 2$, we get $\Delta\mu = 6.4 \text{ kcal mole}^{-1}$, a reasonable figure as compared with interaction energies in hydrogen-bonded alcohols.

¹⁷ A. B. Bestul and S. S. Chang, *J. Chem. Phys.* **40**, 731 (1964).

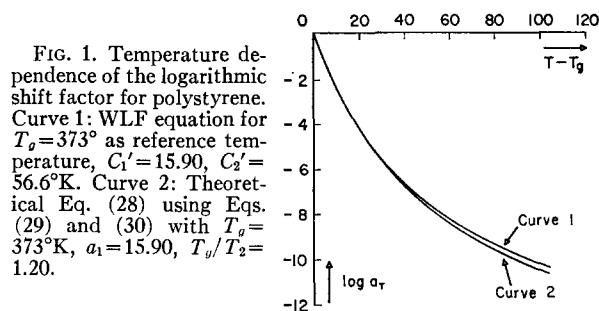


FIG. 1. Temperature dependence of the logarithmic shift factor for polystyrene. Curve 1: WLF equation for $T_g = 373^\circ$ as reference temperature, $C_1' = 15.90$, $C_2' = 56.6^\circ\text{K}$. Curve 2: Theoretical Eq. (28) using Eqs. (29) and (30) with $T_g = 373^\circ\text{K}$, $a_1 = 15.90$, $T_g/T_2 = 1.20$.

sponding figures $\Delta\mu s_c^*/k$ are given in the last column of Table I.

Since the values ΔC_P are not known very precisely, these values for $\Delta\mu s_c^*/k$ are only significant in their order of magnitude. Using as a first estimate $s_c^* = k \ln 2$, one finds values for $\Delta\mu$ which are well in the range of molecular interaction energies. In the case of polymers the hindrance energies of internal rotations are expected to be of the order of a few kilocalories per mole. The comparatively higher values for $\Delta\mu$ in the case of the higher alcohols and glucose reflect the situation that here every molecule is bound to its neighbors by several hydrogen bonds, as can be inferred from x-ray data afforded by the corresponding crystals.¹⁸

To check the temperature dependence of the theoretical parameter a_2 we have plotted the shift factor for polystyrene in Fig. 1. Curve 1 gives the WLF Eq. (1) with $T_g = 373^\circ\text{K}$; $C_1 = 15.90$; $C_2 = 56.6^\circ\text{C}$. Curve 2 gives the theoretical Eq. (28) with $T_g = 373^\circ\text{K}$; $a_1 = 15.90$ and a_2 given by Eq. (31) with $T_g/T_2 = 1.20$ (see Table I). The maximal deviation between the two curves is less than 4%.

This coincidence of the empirical WLF equation and the molecular kinetically derived equation suggests that the essence of the relaxation behavior in the melt can indeed be depicted by cooperative transitions where the size of the cooperatively rearranging region is determined by the configurational entropy.

ZERO-POINT ENTROPY OF THE GLASS

The ratio T_g/T_2 can also be determined calorimetrically from the zero-point entropy of the glass. According to the equilibrium theory of Gibbs and DiMarzio,⁹ the configurational entropy at T_2 is zero. Now, if we neglect differences in vibrational entropy between the hypothetical glass at T_2 and the crystal at T_2 , the zero-point entropy ΔS_0 , i.e., the apparent entropy difference between glass and crystal at $T = 0^\circ\text{K}$ should be equal to the configurational entropy of the liquid that was "frozen in" at T_g

$$\Delta S_0 = (S_{\text{glass}} - S_{\text{cryst}})_{T=0} = S_{\text{config}}(T_g). \quad (34)$$

¹⁸ T. R. R. McDonald and C. A. Beevers, *Acta Cryst.* **3**, 394 ff. (1950).

TABLE II. Comparison of the ratios T_g/T_2 derived from calorimetric and viscosimetric measurements.

	$(T_g/T_2)_{\text{calorimetric}}$	$(T_g/T_2)_{\text{viscosimetric}}$
Hevea rubber	1.22	1.40
Glycerol	1.26	1.45
<i>n</i> -Propanol	1.37	(3.93)

On the other hand, since $\Delta C_P = C_{P \text{ melt}} - C_{P \text{ glass}}$ is the configurational part of the specific heat, we have

$$S_{\text{config}}(T_g) = \int_{T_2}^{T_g} \frac{\Delta C_P}{T} dT. \quad (35)$$

Thus, if ΔC_P and ΔS_0 are known from calorimetric measurements, one can calculate from Eqs. (34) and (35) the numerical value of T_g/T_2 .

Calculations of this kind were first done by Passaglia and Kevorkian.^{19,20} These authors evaluated the zero-point entropy of the amorphous regions in the semi-crystalline polymers polyethylene and polypropylene but could only locate the glass temperature properly in the case of polypropylene. For amorphous polypropylene Passaglia and Kevorkian derived¹⁹

$$\begin{aligned} T_g/T_2 &= 1.26, \\ T_g - T_2 &= 53^\circ\text{C}, \end{aligned}$$

which is in excellent agreement with the average values derived above from relaxation in glass-forming liquids.

Bestul and Chang¹⁷ have performed the numerical analysis for eleven different glass-forming materials approximating ΔC_P as temperature independent between T_2 and T_g . The mean value of T_g/T_2 for these data and the average deviation from this mean value is

$$T_g/T_2 = 1.29 \pm 10.9\%. \quad (36)$$

The coincidence with our value T_g/T_2 from viscosity measurements is striking, especially in view of the fact that the calorimetric data used by Bestul and Chang mostly refer to compounds different from those considered in Table I. There are only three substances for which the values of T_g/T_2 have been obtained both from zero-point entropy by Bestul and Chang and

¹⁹ E. Passaglia and H. K. Kevorkian, *J. Appl. Polymer Sci.* **7**, 119 (1963).

²⁰ E. Passaglia and H. K. Kevorkian, *J. Appl. Phys.* **34**, 90 (1963).

from viscosimetric data. The data for these are reproduced in Table II. Again with the exception of *n*-propanol, the agreement within these pairs of values is satisfactory.

CONCLUSIONS

The molecular-kinetic theory proposed in the present paper explains the temperature dependence of relaxation phenomena in glass-forming liquids essentially in terms of the temperature dependence of the size of the cooperatively rearranging region.

The size of this cooperative region is shown to be determined by the configuration restrictions associated with amorphous packing that can be described by the configurational entropy of the melt.

The result of the theory is a relation which practically coincides with the empirical WLF equation. The parameters of this equation depend on the choice of reference temperature T_s , its ratio T_s/T_2 to the equilibrium second-order transition temperature T_2 , and the product, $\Delta\mu s_c^*/(\Delta C_P)$, of a Gibbs-free-energy barrier (restricting internal rotation) per molecular segment, the critical configurational entropy necessary for the cooperative region to move, and the reciprocal of the difference between the specific heat of the melt and that of the glass at T_g .

From the comparison of theoretical and experimental results the parameters T_g/T_2 and $\Delta\mu s_c^*$ can be evaluated.

The ratio T_g/T_2 determined in this way shows a remarkable constancy for widely differing substances, thus verifying the expected close correlation between T_g and T_2 .

Values of T_g/T_2 determined from calorimetric measurements of the zero-point entropy are of nearly the same magnitude as those obtained from the viscosimetric data.

The values of $\Delta\mu s_c^*$ derived from the relaxation data are of the order of magnitude to be expected from our knowledge of molecular interactions.

We may conclude, therefore, that the kinetic properties of glass-forming liquids within roughly 100°C of the glass temperature can be explained satisfactorily in terms of the thermodynamic properties of the equilibrium melt.

Thus, the apparent conflict of the need for a largely kinetic and the need for an essentially thermodynamic interpretation of the glass transition seems to be resolved.