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Nature of the Glass Transition and the Glassy State

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The thermodynamic properties of amorphous phases of linear molecular chains are obtained from statistical mechanics by means of a form of the quasi-lattice theory which allows for chain stiffness and the variation of volume with temperature. A second-order transition is predicted for these systems.

This second-order transition has all the qualitative features of the glass transition observed experimentally. It occurs at a temperature which is an increasing function of both chain stiffness and chain length and a decreasing function of free volume.

The molecular "relaxation times" are shown to increase rapidly as the second-order transition temperature is approached from above.

To permit quantitative application of the theory and determine the relationship between the second-order transition and the glass transition observed in "slow" experiments these two transitions are tentatively identified. By this means quantitative predictions are made concerning the variations of (1) glass temperature with molecular weight, (2) volume with temperature, (3) volume with molecular weight, (4) volume at the glass temperature with the glass temperature for various molecular weights of the same polymer, (5) specific heat vs temperature, and (6) glass temperature with mole fraction of low-molecular weight solvent, since extensive experimental results are available for these properties. These and other theoretical predictions are found to be in excellent agreement with the experimental results.

I. INTRODUCTION

A SOLID phase is ordinarily designated as a glass if it is noncrystalline and exhibits what appears to be a second-order transition (in the sense of Ehrenfest) often referred to as the glass transition, at some higher temperature.

Although the glassy state is thus defined in terms of thermodynamic variables, it is not necessarily implied that the glassy state is one of even metastable (with reference to a possible crystalline phase) equilibrium. In fact characteristic relaxation times for molecular motions (as determined by viscoelastic and dielectric studies) are so large near the glass temperature that the value obtained for the latter may depend on the time scale of the experiment by which it is measured. The predominance of relaxation effects in the vicinity of the glass temperature has led some authors to assume that the very existence of the apparent second-order transition is a result of these admittedly unexplained peculiarities in viscoelastic behavior.

On the other hand, difficulties arise in a purely kinetic view of the glass transition. Kauzmann has shown that, if the thermodynamic behavior observed experimentally in a material above its glass temperature is extrapolated through and below the glass temperature, to obtain the supposed equilibrium behavior at these lower temperatures, absurd results, such as negative entropies, are obtained.

Similar extrapolations may be obtained theoretically from the statistico-mechanical theory of semiflexible chains developed by Flory (in a paper which was primarily concerned with solutions of readily crystallizable polymers rather than with glass forming systems) if results based on an approximation known to be valid at high temperatures are applied at low temperatures.

1 P. Ehrenfest, Leiden Comm. Suppl. 756 (1933).

Invocation of prior crystallization is a means of avoiding this difficulty in some cases. However, certain materials, such as atactic vinyl polymers, have, as their lowest energy conformations, shapes that cannot pack in a regular array. Furthermore, many polymers are easily supercooled. A resolution of the paradox, rather than mere avoidance of it, is apparently required.

Another shortcoming of current, purely kinetic, views of the glass transition is their failure to explain the kinetic phenomena themselves. Surely a description of the (metastable) equilibrium structure of the supercooled liquid phase approaching its glass temperature from above is a prerequisite to an understanding of its viscoelastic and dielectric sluggishness in this region.

In any event, we can categorically state that a glass-forming material has equilibrium properties (though they may be difficult to realize), and we may reasonably ask what they are. The present article is addressed to this question. The theory given below will, in fact, predict that a second-order transition can be observed even if the attainment of equilibrium is not prevented.

Furthermore, we will see that, as we decrease the temperature of a glass forming material to this second-order transition temperature, the number of states available to the system decreases sharply, so that there must be a drastic variation in kinetic (viscoelastic and dielectric etc) properties. Thus the very equilibrium properties of the supercooled liquid give rise to kinetic sluggishness which may prevent the equilibrium second-order transition point from being reached by an equilibrium phase in an experimentally realizable amount of time. The actual amount of time required for the attainment of equilibrium near the second-order transition point cannot, however, be calculated from an equilibrium theory alone.

A preliminary announcement of this conclusion is contained in reference 3.

Throughout this paper we refer to the transition predicted theoretically as the second-order transition and the transition observed experimentally as the glass transition.
Nevertheless, for two reasons it is useful to examine the agreement between theoretical and experimental results which is afforded by tentative identification of the glass transition point (observed experimentally) with the (theoretical) second-order transition point: (1) Reasonably good agreement would support the contention of the theory that the thermodynamic second-order transition temperature is a lower limit, which must exist and which is obtained in experiments of infinite time scale, to the value of the glass temperature which can be observed experimentally, and (2) excellent agreement would suggest that the theoretical (thermodynamic) point and the experimental (at least partially though not fundamentally kinetic) point observed in "slow" experiments are close enough, or at least sufficiently stringently related, so that the two may be profitably viewed as one and the same.

The principal requirements for the existence of the (theoretical) second-order transition in any given material are molecular asymmetry and chain stiffness, the more elongated the molecule the higher the second-order transition temperature, and the stiffer the molecule the higher the second-order transition temperature. Therefore, successful identification of this transition with the glass transition would point to these properties as the principal criteria for glass formation.

The calculations of Flory, which will be utilized in this discussion, are based on the familiar Meyer-Flory-Huggins lattice model but depart from previous work in that they allow for the effects of chain stiffness to the extent that the latter may be approximated in a way which is strictly accurate only when said stiffness arises solely from nearest neighbor interactions along the molecular chains.

A more general treatment, in which the nature of the restriction to rotation around any given chain bond is allowed to depend on the conformation of the rest of the molecule, also predicts the existence of a second-order transition. However, its quantitative application requires currently unavailable knowledge of many molecular energy levels. Therefore, we will utilize, as a framework for the present discussion, a method based on the nearest neighbor approximation, which reduces to one the number of intramolecular (stiffness) energy parameters, in order to be able to effect a quantitative comparison of the properties of the two transition points in question.

The more general treatment can be applied to cross linked and ringed systems as well as systems composed exclusively of linear chains and, in fact, predicts a second-order transition for these systems as well. However, most of the well-controlled experiments investigating the glass transition have been carried out with systems of synthetic organic linear polymers which are simpler and easier to characterize chemically. Furthermore, the method involving the nearest neighbor approximation is only applicable to linear chains. Therefore we restrict the present discussion of the relation between the second-order and glass transitions to these linear systems.

II. PARTITION FUNCTION AND THE SECOND-ORDER TRANSITION

We consider a system composed of $n_x$ linear chains of $x$ monomer segments each ($x$-mers). In common with usual practice we assume that all the allowed conformations of a molecular chain fit on a lattice whose sites are of such a size as to accommodate a maximum of one chain segment apiece. We allow for vacant sites and designate their number as $n_v$. If the number of primary valences of each of the atoms constituting the chain backbone is $z$ (for example, for carbon $z=4$) there are $(z-1)$ possible (reasonably low energy) orientations of a bond, $i$, with respect to the coordinate system formed by the bonds, $i-1$, $i-2$ of the same molecule ($i\neq 1, 2$). We will associate an energy, $e_i$, with one of these orientations and an energy, $e_2$, with each of the $z-2$ remaining orientations.

The total intramolecular (flex) energy is

$$E = f e_2(x-3)n_x + (1-f) e_1(x-3)n_v$$

(1)

where $f$ is the fraction of bonds "flexed," i.e., bonds in the orientation of energy, $e_2$.

The intermolecular (hole) energy is proportional to the number of intermolecular "van der Waals bonds" which are broken on the introduction of $n_v$ lattice vacancies,

$$\Phi = e_2\alpha n_v x^2/2$$

(2)

where $\alpha$ is the energy of interaction, (the "van der Waals bond" energy) between a pair of chemically

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1 A good list of references to work on this subject is given by P. J. Flory, *Principles of Polymer Chemistry* (Cornell University Press, Ithaca, 1953), Chap. XII.


3 The total number of bonds from which this fraction "flexed," $f$, is calculated is, of course, $(x-3)n_v$, rather than $xn_v$, since "flexing" of the first two bonds of each molecule can be effected without changing the conformation and, therefore, the energy of the molecule.
nonbonded but nearest neighboring segments, \( S' \) is the fraction, \( [ (z'-2) x + 2 ] n_x / [(z'-2) x + 2] n_x + z' n_o \), and \( z' \) is the coordination number of the “best” lattice characterizing the amorphous packing of the system of segments and holes.

For the lattice model to be self-consistent it is not necessary for \( z' \) and \( z \) to be equal, as has been assumed heretofore. It is necessary, however, for each of the \( z-1 \) locations which are permissible (i.e., of low intramolecular energy) for a segment \( i \) of molecule \( f \) after segments \( i-1 \), \( i-2 \), and \( i-3 \) of the same molecule have been located, to be among the set \( z' -1 \) allowed by the lattice structure. Thus, these \( z-1 \) possible locations for segment \( i \) and the sites occupied by the previous \( z-1 \) segments of the chain, and in fact all sites which the chain could conceivably occupy after its general location and orientation are specified by location of its first three segments, are members of a lattice of coordination number \( z \) which is a sublattice of coordination number \( z' \). Furthermore, since molecule \( j \) could have been located and oriented, by location of its first three segments, anywhere in the major lattice of coordination number \( z' \), every site of the latter must be a member of a sublattice of coordination number \( z \). Of course, the superposition of all the sublattices of coordination number \( z \) is the major lattice of coordination number \( z' \).

A particularly useful example is the set of tetrahedral sublattices of coordination number 4 which add up to a body centered cubic lattice of coordination number 8.

Since the best lattice for an individual polymeric chain containing carbon atoms in its backbone is the tetrahedral lattice, we will use \( z=4 \) in our numerical calculations. On the other hand, in the absence of any specific information concerning the best value for \( z' \) in a polymeric system, we simply use \( z'=z \), rather than carry \( z' \) along as an extra parameter.

The thermodynamic properties of this system can be found by consideration of a canonical ensemble of such systems and evaluation of the resulting partition function. It is convenient to group together all states of the same energy in writing the partition function,

\[
Q = \sum_{W=0}^{W_{\infty}} W(f,n_0) \exp \left[ -\frac{[f(x-3)n_x z_2 + (1-f)(x-3)n_x z_1] + x n_0 S_x / 2}{kT} \right].
\]

Where

\[
W(f,n_0) = \sum_{W=0}^{W_{\infty}} W \exp \left[ -\frac{[f(x-3)n_x z_2 + (1-f)(x-3)n_x z_1] + x n_0 S_x / 2}{kT} \right],
\]

Now, since Flory's expression for \( W \) is essentially\(^{14} \)

\[
Q = Q' - Q'',
\]

where

\[
Q' = \sum_{W=0}^{W_{\infty}} W(f,n_0) \exp \left[ -\frac{[f(x-3)n_x z_2 + (1-f)(x-3)n_x z_1] + x n_0 S_x / 2}{kT} \right],
\]

and

\[
Q'' = \sum_{W=0}^{W_{\infty}} W(f,n_0) \exp \left[ -\frac{[f(x-3)n_x z_2 + (1-f)(x-3)n_x z_1] + x n_0 S_x / 2}{kT} \right].
\]

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\]

where

\[
Q' = \sum_{W=0}^{W_{\infty}} W(f,n_0) \exp \left[ -\frac{[f(x-3)n_x z_2 + (1-f)(x-3)n_x z_1] + x n_0 S_x / 2}{kT} \right],
\]

and

\[
Q'' = \sum_{W=0}^{W_{\infty}} W(f,n_0) \exp \left[ -\frac{[f(x-3)n_x z_2 + (1-f)(x-3)n_x z_1] + x n_0 S_x / 2}{kT} \right].
\]

Now, since Flory's expression for \( W \) is essentially\(^{14} \)

\[
W = \frac{[(x-2) x + 2] n_x + x n_0}{2} \frac{[(x-1) n_x (x-2) / (x-3)]!}{(n_0)!! [(x-2) x + 2] n_x + x n_0} \frac{[(x-2) x + 2] n_x + x n_0}{2} \frac{[(x-1) n_x (x-2) / (x-3)]!}{(n_0)!! [(x-2) x + 2] n_x + x n_0},
\]


\(^{14} \)Flory's expression actually differs from our Eq. (5) in two respects: first, since he was concerned with solutions but not with thermal variations of volume, his expression contains a number, \( n_i \), of solvent molecules in place of our number, \( n_i \), of holes; second, his expression is the result of use of the fraction \( (N_0 - x) / N_0 \) for the expectancy that a specified site is available to a chain segment after \( i \) molecules have already been placed on the lattice, whereas ours is the result of use of the more accurate expression, \( (N_0 - x) / [N_0 - 2(x-1)] / (x-1) \). Originally used by M. L. Huggins, Ann. N.Y. Acad. Sci. 43, 1 (1942). In these expressions \( N_0 \) is the total number of lattice sites.
\[
Q' = \sum_{n_0} \frac{[(z-2)x+2]n_0}{2} \exp \left( -\frac{zx_n S_x}{2kT} \right)
\]

where \( \lambda' \) represents the factor which is summed over \( f \), and \( \mu' \) the factor which is summed over \( n_0 \).

The factor \( \lambda' \) is easily evaluated. Recognizing that each term of \( \lambda' \) is a term of the binomial expansion of \([\exp(-\epsilon_1/kT)+(z-2)\exp(-\epsilon_2/kT)]^a\) multiplied by a common factor, we get

\[
\lambda' = \frac{[\exp(-\epsilon_1/kT)+(z-2)\exp(-\epsilon_2/kT)]^a}{(n_0)!}.
\]

For the "free energy" derived from \( \lambda' \), we have

\[
F'_{\lambda'} = -kT \ln \lambda'.
\]
Below this temperature, \( T_2 \), we must use another method to determine the maximum term allowed in \( Q \) (absent in \( Q' \)). For this purpose we inspect the ratio, \( r \), at any \( T \sim T_2 \) of the term which is the maximum one at \( T_2 \) to any other allowed term,

\[
\frac{1}{W(f_1,n_0)} \exp\left[-\frac{E(f_1,n_0)}{kT}\right] \geq \frac{1}{W(f_1,n_0)} \exp\left[-\frac{E(f_{T_2},n_0)}{kT}\right] \frac{r}{T_2} = \frac{1}{W(f_1,n_0)} \exp\left[-\frac{E(f_{T_2},n_0)}{kT}\right] > 1, \tag{18}
\]

since \( W(f_1,n_0) > 1 \) (allowed term). \( f_{T_2} \) and \( n_0 \) are, of course, the expectation values given by Eqs. (9) and (11) for \( f \) and \( n_0 \) at the temperature \( T_2 \). Thus the ratio of the term which is the maximum one at \( T_2 \) to any other allowed term is even larger at a temperature less than \( T_2 \) than it is at \( T_2 \). This term, for which \( W = 1 \), is, therefore, an even more accurate representation of the total partition function, \( Q \), at these lower temperatures than it is at \( T_2 \).

We may now write for the free energy below \( T_2 \),

\[
S > T_2 = -\frac{\partial F > T_2}{\partial T} = kN \left[ \frac{z-2}{2} \ln \left( \frac{V_0}{S_0} \right) + \frac{n_0}{S_0 \epsilon_2} \ln \left( \frac{V_0 ^{\epsilon_2 - 1}}{S_0 ^{\epsilon_2}} \right) + \left( \frac{x-3}{x} \right) \left[ \ln \left( e^{-\epsilon_2/kT} + (z-2)e^{-\epsilon_1/kT} \right) + \frac{\epsilon_1}{kT} e^{-\epsilon_1/kT} + \frac{(z-2)\epsilon_2}{kT} e^{-\epsilon_2/kT} \right] \right], \tag{20}
\]

and

\[
S < T_2 = -\frac{\partial F < T_2}{\partial T} = 0, \tag{20A}
\]

This temperature \( T_2 \) may readily be obtained from Eq. (21), with the substitutions afforded by (20), (20A), (9), and (11). The result is,

\[
0 = \left( \frac{z-2}{2} \right) \ln \left( \frac{V_0}{S_0} \right) + \frac{n_0}{S_0 \epsilon_2} \ln \left( \frac{V_0 ^{\epsilon_2 - 1}}{S_0 ^{\epsilon_2}} \right) + \left( \frac{x-3}{x} \right) \left[ \ln \left[ 1 + (z-2)e^{-\epsilon_1/kT} \right] + f(\epsilon_2 - \epsilon_1) / kT \right], \tag{22}
\]

where \( V_0 \) and \( S_0 \) are subject to Eq. (11). We see that \( T_2 \) is a function of the flex energy, \( \epsilon_2 - \epsilon_1 \), the hole energy, \( \alpha \), and the molecular weight, \( x \) (degree of polymerization).

Since the functions \( F \) and \( S \) are continuous functions of \( T \) at \( T_2 \) [Eqs. (19) and (21)], the thermodynamic system energy, \( U = F + TS \), is also continuous at \( T_2 \).

The volume of the polymer phase is

\[
V > T_2 = C(T) [x_n + n_0(T)], \tag{23}
\]

\[
V < T_2 = C(T) [x_n + n_0(T_2)], \tag{23A}
\]

where \( C(T) \) is the volume of a lattice site at temperature \( T \), \( n_0(T) \) and \( n_0(T_2) \) are determined by application of Eq. (11).

We note that the volume above \( T_2 \) is independent of the flex energy, \( \epsilon_2 - \epsilon_1 \). Below \( T_2 \), however, the volume is affected by the value of \( T_2 \), which in turn is a function of the flex energy as well as hole energy and molecular weight. Of course, the volume is also a continuous function at \( T_2 \).

On the other hand, since these “first-order” thermodynamic functions, \( F \), \( S \), \( U \), and \( V \), are described by...
different analytical forms in the two temperature regions, their first temperature derivatives, the "second-order" thermodynamic functions, are discontinuous at $T_2$.

For example, using Eqs. (11) and (23) we find that the thermal expansivity is given by

$$\frac{1}{V} \frac{\partial V}{\partial T} > T_2 = \frac{\partial C/\partial T}{C} + \frac{\partial n_0/\partial T}{x_n + n_0} = \frac{\left(\frac{\alpha}{2k_T^2}\right) V_0 S_{x^2}}{C} \frac{\partial C/\partial T}{T},$$

$$\frac{1}{V} \frac{\partial V}{\partial T} < T_2 = \frac{\partial C/\partial T}{C}. \quad (24A)$$

The expressions for the specific heat, $C_P$, are also readily shown to be unequal at $T_2$. We have, therefore, an Ehrenfest second-order transition\(^1\) at the temperature $T_2$, given by Eq. (22).

Let us follow a real polymer system through the point, $T_2$, where the configurational entropy, $S$, is zero. At high temperatures $S>0$, there being many ways for the molecules to be packed together in the bulk phase. At these temperatures the molecules do not prefer any one molecular conformation over any other and can fit themselves into the available tubes of empty volume ($x$ contiguous empty lattice sites per molecule). As we cool the polymer phase, the molecules have less energy to share and two processes occur: (1) low-energy molecular conformations begin to predominate (small $f_{\text{max}}$), and (2) the volume $(n_0 \text{ max})$ decreases. The number of ways in which the molecules may be packed in the bulk phase is reduced, since the tubes of empty volume required by the molecules now begin to satisfy stringent geometric requirements, (x empty lattice sites which are now contiguous in a definite geometric arrangement for each molecule). As we lower the temperature further, the polymer system reaches a point, $T_3$, where (amorphous) molecular packing would be impossible if these two processes continued. The system remains, therefore, in (one of) its configuration(s) of lowest permissible energy, i.e., the "ground state" of amorphous packing.

This "ground state" may of course be degenerate. Had we used an exact method for evaluating $W$, we might well have found this to be the case. In our approximate treatment we found it convenient to use $W=1$ as the lower limit to the summation, (3), and therefore $W_{\text{max}}=1$ as the criterion for $T_3$, but use of reasonable (small compared to $x_n$) values of the degeneracy of this ground state\(^1\) would make a negligible change in the value obtained for $T_2$. Strictly speaking, any of the system states may still be occupied, the relative occupation probabilities in our canonical ensemble being given by the terms of Eq. (3). However, as has been demonstrated, only a few of the states occur with a nonnegligible probability.

Furthermore, the (free energy) barrier restricting flow of a system from one of these states (configurations) to another is very high in the neighborhood of $T_2$, and at all temperatures below $T_2$, because, in this region (of temperature), the few states that could conceivably occur are widely separated in phase space, and proceeding from one to another involves a considerable change in the topology of the molecular entanglements. Thus we may expect the system to respond only sluggishly to any change in any of the external forces applied to it in this temperature region. Relaxation times characterizing viscoelastic and dielectric response should become very long as $T_3$ is approached from above.

III. COMPARISON OF THE SECOND-ORDER TRANSITION WITH THE GLASS TRANSITION

We wish to compare the consequences of the foregoing equations with experimental results. For this we assume that our second-order transition temperature, $T_2$, may be identified with the glass transition temperature, $T_G$, which is observed experimentally. Henceforth, we replace $T_2$ in the previous equations with $T_G$.

We discuss first the monodisperse phase of pure $x$-mers, to which all the equations of Sec. II apply directly without any extension or modification, and then proceed to a discussion of polydisperse systems and solutions.

A. Monodisperse Phase of Pure X-Mers

In order to apply the equations of Sec. II to a particular material we need to know $\alpha$ and $(\epsilon_2-\epsilon_1)$ for the specification of the lower limit to $W$, and therefore $S<T_0$, without affecting the location of $T_2$ [Eq. (22)]. The degeneracy arising from the distinguishability of atactic molecular chains is assumed to be primarily of this second type and is thus neglected in Sec. III.
that material. α is easily determined by

$$\lim_{\delta \to 0} \left[ \frac{1}{V} \frac{\partial V}{\partial T} \right]_{T_G + \delta} - \left[ \frac{1}{V} \frac{\partial V}{\partial T} \right]_{T_G - \delta} = \frac{\partial n_0/\partial T}{x n_0 + n_0} T_G$$  \hspace{1cm} (25)

and Eq. (24). (ε₂ - ε₁) is easily obtained from Eq. (22) and the experimental value for the glass temperature.

If we wish to predict volume changes above \( T_a \), we must also have information concerning \( C \). Since

$$\lim_{T \to T_G} \left( \frac{\partial C/\partial T}{C} \right)_{T < T_G} = \lim_{T \to T_G} \left( \frac{\partial C/\partial T}{C} \right)_{T > T_G},$$  \hspace{1cm} (26)

we may expect that the expression, \( \partial C/\partial T/C = \text{constant} \), which describes \( C \) well below \( T_G \), may be used as a guide to extrapolation of \( C \) values through and above \( T_G \).

The following quantities have been found experimentally by Fox and Flory\(^{17} \) for polystyrene of molecular weight 85,000 \((x = 1640)\).

$$\left( \frac{1}{V} \frac{\partial V}{\partial T} \right)_{T < T_G} = 2.2 \times 10^{-4} \text{cal/K.} \hspace{1cm} (27)$$

$$T_G = 373^\circ \text{K.} \hspace{1cm} V_{T_G} = 0.969 \text{ ml/g.}$$

By use of Eqs. (11), (22), (23), and (24) we get

$$\frac{2\alpha}{k} = 887.7^\circ \text{K}$$

$$\frac{(\epsilon_2 - \epsilon_1)}{k} = 839.3^\circ \text{K}$$  \hspace{1cm} (28)

$$x n_0 C = 0.86274 \exp(2.2 \times 10^{-4} T) \text{ ml/g.}$$

A plot of the glass temperature as a function of molecular weight (or \( x \)) affords a good test of the theory (and the hypothesis, \( T_2 = T_G \)) because the glass temperature, not being directly dependent on either the internal vibrational degrees of freedom of each molecular conformation or the lattice site size, \( (C) \), is a function of only the principal parameters of the theory, \((\epsilon_2 - \epsilon_1)\) and \( \alpha \). This plot is shown in Fig. 1. Remembering that at extremely high \( x \), not shown on the graph, the theoretical and experimental values of \( T_G \) coincide

\(^{16}\) The equation, \( \partial C/\partial T/C = \text{constant} \), works equally well.

The principal factor responsible for the variation of methacrylates, for which light scattering studies indicate roughly the abscissa. The experimental measurements were made on samples which were obtained by fractionation systems or, as we shall see below, polydisperse systems.

The theoretical curve pertains to mono disperse to perfectly homogeneous polymer chains, whereas the number average molecular weights are given on the abscissa. The theoretical curve refers to mono disperse to perfectly homogeneous polymer chains, whereas the number average molecular weights are given on the abscissa. The theoretical curve refers to perfectly homogeneous polymer chains, whereas the number average molecular weights are given on the abscissa.

The configurational entropy plays, of course, a central role in the theory; since it is simply related to the number of configurations, \( W \). For this reason we show a plot of its theoretical variation with temperature (Fig. 5), even though there are no experimental data to be presented for comparison. The dashed line is the result obtained if the formula, \( S > T_G \), is used (incorrectly) below \( T_G \). If, of course, the identification of \( T_2 \) and \( T_G \) is valid, this dashed line is the (invalid) theoretical counterpart of Kauzmann’s extrapolations through and below \( T_G \) of the experimental data obtained above \( T_G \). The inapplicability of \( S > T_G \) in this

Fig. 2. Theoretical variation (the curve) of specific volume with temperature for polystyrene of molecular weight 85,000 and the experimental points (the three circles) of Fox and Flory.\(^{17}\)

At the same time it lowers the value of the difference, \( \epsilon_2 - \epsilon_1 \), between the energies of the “best” rotational positions (the potential energy minima).

In cases where the values of \( \epsilon_2 - \epsilon_1 \) are nearly alike for two linear chains of the same \( x \), the values of the “free volume,” \( n_0 \), may determine which has the higher glass temperature.\(^{19}\) According to the present theory, then, certain of the various hypotheses relating free volume and glass temperature\(^{20}\) may be true in a restricted sense (however, see below).

The extensive dilatometric studies of the variation of specific volume with varying temperature and varying molecular weight\(^{19,21}\) provide another test of our attempted identification of \( T_2 \) with \( T_G \). A curve representing the variation of \( V \) with \( T \) is shown in Fig. 2. The most interesting thing about the plot is the definite (concavely) upward curvature, which arises from the variation of \( n_0/\pi n_x \) with temperature. This strongly suggests that a straight line should not be used to represent the experimental data.\(^{21}\)

Curves of \( V \) vs \( x \) for two temperatures are shown in Fig. 3. They show the right qualitative behavior but give specific volume values for low molecular weights which are lower than the corresponding experimental values. The theoretical curve pertains to monodisperse systems or, as we shall see below, polydisperse systems whose number average molecular weights are given on the abscissa. The experimental measurements were made on samples which were obtained by fractionation and whose “viscosity average molecular weights” are given on the abscissa. The theoretical curve also refers to perfectly homogeneous polymer chains, whereas the

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\(^{17}\) S. S. Rogers and L. Mandelkern, in J. Phys. Chem. 61, 985 (1957), have recently proposed that the free volume is the principal factor responsible for the variation of \( T_G \) in the poly-\( \alpha \)-alkyl) methacrylates, for which light scattering studies indicate roughly equal chain stiffnesses.

\(^{20}\) A collection of appropriate references is given in reference 19.


\(^{18}\) Fox and Flory\(^{17}\) have suggested this on observation of their experimental data on polystyrene.

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Fig. 3. Theoretical variation (the curves) of specific volume with molecular weight (in units of \( x \)) for two temperatures, 140°C and 217°C, and the corresponding experimental data (circles) of Fox and Flory. The upper circles were actually obtained from a curve which best fits the experimental data.
region is, then, the resolution of Kauzmann's negative (configurational) entropy paradox since this negative entropy is not obtained for $S_{<T_G}$.

Specific heat data are available in the cases of polystyrene and polyisobutylene. However, the specific heat is sensitive to any disparity in the energies of the $(z-2)$ possible high-energy orientations of each chain bond, so that the assumption that a single, average value, $e_2$, may be used for them all affects adversely the quantitative agreement which may be obtained between theoretical and experimental results for this property.

Nevertheless about 60% of the magnitudes observed experimentally for the specific heat discontinuities of these compounds at their glass temperatures may be obtained theoretically with this assumption, the value of $(e_2-e_1)$ used being, as before, that which locates $T_G$ properly. It may be shown that use of this assumption yields a lower limit to the magnitude of the specific heat discontinuity.

Furthermore, the qualitative features of the specific heat behavior above and below $T_G$ are given correctly by the theory even with this assumption. If this assumption is removed, and allowance is made for the inequality of the energies of the (two) higher energy bond orientations, the whole configurational specific heat curves can be fitted quantitatively.

### B. Polydisperse Systems and Solutions

When all the molecules of the system do not have the same chain length, $x$, the evaluation of the partition function may be carried out by the same method as in the monodisperse case but is a bit more tedious though no more difficult. A particularly simple result may easily be obtained when all the molecules have a chain length greater than two, however. This relates the thermodynamic functions of such a polydisperse system, containing $n_\i$ $i$-mers where $i$ runs from 3 to $\infty$, to those of a monodisperse system of $n_\x$ $x$-mers, the "number average" chain length, $\bar{x}$, being defined by

$$\bar{x} = \sum_{i=3}^{\infty} i n_\i / n_\x$$

where

$$n_\x = \sum_{i=3}^{\infty} n_\i.$$  

Furthermore, even if these energies are sufficiently close together for an average to be acceptable, it is not the same average as that which determines the glass temperature. Therefore we still should not expect our value of $(e_2-e_1)$ determined from the glass temperature, to give the correct value for the specific heat discontinuity.

If the "potential energy well" whose bottom is $e_1$ has a shape (force constant) different from that whose bottom is $e_2$, the contribution to the specific heat of bond librations in these wells is also discontinuous at $T_G$. In such a case this discontinuity would also have to be evaluated if good agreement with experimental results were desired.

25 Furthermore, the qualitative features of the specific heat behavior above and below $T_G$ are given correctly by the theory even with this assumption.

26 To fit the whole curve, rather than just the discontinuity at $T_G$, the contributions to the specific heat of intramolecular vibrations (and librations) must be estimated. This is best done by appropriate extrapolation of the specific heat curve found experimentally below $T_G$ (where there is no configurational specific heat) to temperatures above $T_G$.

27 In the mental process of feeding molecules into the lattice, implicit in the Flory counting procedure, it is convenient to feed in molecules of the same degree of polymerization in succession, proceeding to another degree of polymerization only when these have been exhausted; this ensures the grouping of factors which permits simplification of the expressions obtained.
To see this we evaluate the intramolecular energy as

\[
E = f \sum_{i=3}^{\infty} (i-3)n_i e_i + (1-f) \sum_{i=3}^{\infty} (i-3)n_i e_{i1},
\]

the intermolecular energy as

\[
\Phi = s a n_0 S_0^2 / 2,
\]

where

\[
S_0 = \frac{\sum_i [(x-2)i+2]n_i}{\sum_i [(x-2)i+2]n_i + s n_0}.
\]

and the number of configurations,

\[
W(f,n_0,n_1,\ldots) = W(f,n_0,n_1,\ldots) \prod_{i=3}^{\infty} (n_i)!.
\]

Thus, except for an ordinarily small correction which accounts for an entropy of mixing of the various chain lengths, the thermodynamic properties in this case of a polydisperse system depend on the variables of the system in the same fashion as in the previous case of a monodisperse system with the number average molecular weight now replacing the single molecular weight encountered before.

Ueberreiter and Kanig have, in fact, discovered experimentally that the glass temperature and specific volume of polystyrene samples are functions of the number average molecular weights of the samples. When a polymer sample is dissolved in a solvent of low molecular weight for which \(i=1\) or \(i=2\), the situation is somewhat different. Although the contribution to the partition function of all species for which \(i=2\) is the same as that of an equivalent number, \(n_0\), of dissolved \(x\)-mers (\(x\) and \(n_0\) still being defined by the sums, (29) and (29A)), from \(i=3\), to \(i=\infty\), the contribution of the low-molecular weight solvent remains to be evaluated. If the solvent molecules are single site occupiers (\(i=1\)) their effect on \(W\) is similar to that of an added number, \(n_1\), of holes, except for a factor (\(n_1+n_0\))!

29 This can be seen from the following considerations. Since (1) all segments of each molecule, except the first and second ones counted of each, enter into the counting of the number of configurations of the system in the same way, (2) the first segment of each molecule enters into the counting in the same way as the first segment of each other molecule, and (3) a similar statement holds for the second segments of the molecules, systems with identical numbers of "first segments," identical numbers of "second segments," and the same total number of segments can, according to this counting procedure, be packed on the lattice in the same way. Thus, the number of modes of packing depends on \(x\) and \(n_0\) in the case considered here in the same way as it depended on \(x\) and \(n_1\) in the monodisperse case. However, the fraction of this number of ways of packing on the lattice which are distinguishable from others will be a function of the molecular weight distribution according to the second factor of the right-hand member of Eq. (32).

(n_1)! (n_0)! accounting for the number of ways the \(n_1\) solvent molecules and \(n_0\) holes may be assigned to the \(n_1+n_0\) sites which remain empty after all the polymer molecules have been placed on the lattice.

Alexandrov and Lazurkin have studied the plasticization of polystyrene by styrene monomer. For this solvent (plasticizer) \(i=2\). The expression for the second-order transition temperature in this system is

\[
0 = \frac{\alpha z}{x} \ln \left( \frac{z}{2} \right) + \left( \frac{n_0}{x n_0^2 / 2} \right) \ln \left( \frac{V_0^{1/2} - 1}{S_0^{1/2}} \right) + \frac{1}{2} \left( \frac{z_n}{x} \right) \ln \left[ (z-2)^2 + 2(z-1)/2 \right] + (z-3)n_0
\]

and

\[
W = n_0 / \bar{x} n_0 + n_0, \quad S_0 = s n_0 / \left[ (z-2)^2 + 2 \right] n_0 + s n_0.
\]

In Fig. 6 we show, along with the experimental data, a plot of this theoretical result as a function of percent monomer (styrene), 100 \(2m_a / \bar{x} n_0\), the values of \((e_2-e_1)\) and \(\alpha\) being the same as before. The lower curve is the result obtained when holes are neglected entirely (\(n = \infty\)). It may be seen that these curves afford a good representation for the experimental data.

This lowering of the glass temperature which accompanies the absorption of solvent has an interesting corollary. Since, just as in the previous case of a pure \(x\)-mer phase, the fraction of bonds flexed in the glassy state, \(f > 0\), given by a formula identical to (9) except for the replacement of \(T\) with \(T_{c0}\), \(f < T_0\) is dependent, through \(T_{c0}\), on the variables, such as percent monomer and chain length, which influence \(T_{c0}\). A similar statement may be made concerning the number of holes in the glassy state, \(n_{c0}\).

\[\text{In} 43, 376 (1944).\]

\[\text{U.R.S.S.} 43, 376 (1944).\]
Kargin\textsuperscript{33} has, in fact, discovered experimentally that not only is there a significant heat evolved on absorption of ethyl benzene by glassy polystyrene, but also that this heat is greater for polystyrene samples of high molecular weight than for those of lower molecular weight (and, of course, lower $T_G$). Attributing this heat to the changes in $f$ and $n_o$, we find the same qualitative behavior. The state of affairs as regards quantitative results is, as would be expected, similar to that found previously for the specific heat in the case of pure x-mers.

The decrease in the (partial) molar volume of polymer on its absorption of monomer, which is expected theoretically because of the variation of $n_o$ with $n_2$, has been observed by Kovacs.\textsuperscript{34}

\section*{IV. DISCUSSION}

The results of Sec. III indicate that the glass transition is, in fact, the experimental manifestation of the second-order transition predicted theoretically in Sec. II.

It cannot be concluded unequivocally, however, that the value found for $T_G$ in an experiment of finite time scale is the same as that of $T_2$. There is also the possibility that the values of $T_G$ and $T_2$ are strictly related (for $T_G$ measurements of a specified time scale, of the order of hours say) but not identical. If the relation between them were of the proper mathematical form, $T_G$ and $T_2$ would still exhibit similar properties and vary in the same way with alteration of the values of the independent variables of the system (e.g., $x$, $n_1$).\textsuperscript{35} This possibility cannot be adequately treated in the absence of knowledge of that quantitative relation between them which is to be expected theoretically. We may hope that the qualitative understanding of the

\[ T_G - T_2 = a \quad \text{and} \quad T_G/T_2 = b, \]

where $a$ and $b$ are constants, have been tried in place of the relation $T_G = T_2$ in the procedures of Sec. III. The former works fully as well as $T_G = T_2$ even if $a$ is as large as 50$^\circ$C, but the latter is somewhat less successful.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{The variation of glass transition temperature with solution composition for solutions of polystyrene in styrene monomer. The derivation of the upper theoretical curve allowed for the effect of "holes" whereas that of the lower one did not. The points are the data obtained experimentally by Alexandrov and Lazurkin.\textsuperscript{36}}
\end{figure}

\textsuperscript{33} V. A. Kargin, J. Polymer Sci. 23, 47 (1950).
\textsuperscript{34} A. Kovacs, Compt. rend. 235, 1127 (1952); 235, 1648 (1952).
\textsuperscript{35} The relations $T_G - T_2 = a$ and $T_G/T_2 = b$, where $a$ and $b$ are constants, have been tried in place of the relation $T_G = T_2$ in the procedures of Sec. III. The former works fully as well as $T_G = T_2$ even if $a$ is as large as 50$^\circ$C, but the latter is somewhat less successful.

\textsuperscript{36} The relations $T_G - T_2 = a$ and $T_G/T_2 = b$, which the present equilibrium theory affords, will lead to a quantitative (nonequilibrium) theory for this sluggishness in the near future.

We know, however, that whatever the quantitative relation between $T_G$ and $T_2$ may turn out to be, it has the following qualitative property. $T_2$ is the lower limit, observed in experiments of infinite time scale, to the range of $T_G$. If, as the present results of the quasilattice model indicate, this lower limit does exist, the existence of glasses is not dependent on kinetic phenomena, and we may properly resuscitate the concept of the glassy state as a fourth state of matter.

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