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Julian H. Gibbs, and Edmund A. DiMarzio

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Nature of the Glass Transition and the Glassy State

JULIAN H. GIBBS AND EDMUND A. DIMARZIO
Research and Development Division, American Viscose Corporation, Marcus Hook, Pennsylvania

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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[1]) 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[2] 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[3] from the statistico-mechanical theory of semiflexible chains developed by Flory[4] (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.

Invocation of prior crystallization is a means of avoiding this difficulty in some cases.[2,4] 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.[3]

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.[5]

Furthermore, we will see that, as we decrease the temperature of a glass forming material to this second-order transition[6] 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.

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

[2] W. Kauzmann, Chem. Revs. **43**, 219 (1948).

[3] J. H. Gibbs, J. Chem. Phys. **25**, 185 (1956).

[4] P. J. Flory, Proc. Roy. Soc. (London) **A234**, 60 (1956).

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

[6] 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[7] 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,[8] 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[8] 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.[9]

II. PARTITION FUNCTION AND THE SECOND-ORDER TRANSITION

We consider a system composed of n_x linear polymer chains of x monomer[10] segments each (x-mers). In common with usual practice[7] 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_0. 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, ϵ_1, with one of these orientations and an energy, ϵ_2, with each of the $z-2$ remaining orientations.[11]

The total intramolecular (flex) energy is

$$E=f\epsilon_2(x-3)n_x+(1-f)\epsilon_1(x-3)n_x, \tag{1}$$

where f is the fraction of bonds "flexed,"[12] i.e., bonds in the orientation of energy, ϵ_2.

The intermolecular (hole) energy is proportional to the number of intermolecular "van der Waals bonds" which are broken on the introduction of n_0 lattice vacancies,

$$\Phi=z'\alpha n_0 S_x'/2, \tag{2}$$

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

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[7] 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.

[8] E. A. DiMarzio and J. H. Gibbs, "Chain stiffness and the lattice theory of polymer phases," J. Chem. Phys. (to be published).

[9] The present discussion will actually be restricted to the case of linear homopolymers. Copolymers have been treated, but, since this treatment in its best form requires use of the more general theory (see reference 8), it will not be given here, although its agreement with experimental results is excellent.

[10] The word "monomer" here refers to that unit which is considered to occupy one lattice site. This will ordinarily be one chain backbone atom plus the side groups attached to it as long as the latter are sufficiently small.

[11] The assumption of equal energies for the $z-2$ higher energy orientations is made to simplify the presentation and to reduce the number of intramolecular energy parameters to one, that is $\epsilon_2-\epsilon_1$ (the separate absolute values of ϵ_1 and ϵ_2 will not be required).

The energy, ϵ_2, assigned to the higher energy orientations may be conceived as an average over the $z-2$ actually disparate values. None of the qualitative conclusions of this paper are affected by our use of this assumption. Except for the specific heat, none of the quantitative results are significantly affected as long as the disparity in the energies of these $(z-2)$ higher energy orientations does not exceed 30% of the difference between their average value, ϵ_2, and the energy of the lowest energy orientation, ϵ_1.

[12] The total number of bonds from which this fraction "flexed," f, is calculated is, of course, $(x-3)n_x$, rather than xn_x, 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_x' is the fraction,[13] $[(z'-2)x+2]n_x/[(z'-2)x+2]n_x+z'n_0$, 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 j 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 $i-1$ 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 that 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,

$$Q=\sum_{\substack{W=1\\ f,n_0}}^{W=\infty} W(f,n_0)\exp\left\{-\frac{[f(x-3)n_x\epsilon_2+(1-f)(x-3)n_x\epsilon_1]+z\alpha n_0S_x/2}{kT}\right\}. \tag{3}$$

$W(f,n_0)$ is the total number of ways we can pack the n_x x-mers on the lattice of xn_x+n_0 sites when the total number of "flexed" bonds in each arrangement is $f(x-3)n_x$. If W were to be calculated exactly it would be unnecessary to express explicitly the condition $[W(f,n_0)=1]$ for the lower limit, to the values of f and n_0 over which the summation is taken, since the discrete function, $W(f,n_0)$ could only assume integral values (including zero). However, the analogous quantity in the case where n_0 represents a number of solvent molecules, rather than a number of holes, has been evaluated approximately as a function which runs from 0 to ∞ by Flory,[4] and we wish to use his result. The values of W which are less than unity correspond to no states of the system at all and must be discarded.

To avoid the difficulty presented by the lower limit we write Q in the form

$$Q=Q'-Q'', \tag{4}$$

where

$$Q'=\sum_{\substack{W=0\\ f,n_0}}^{W=\infty} W(f,n_0)\exp\left\{-\frac{[f(x-3)n_x\epsilon_2+(1-f)(x-3)n_x\epsilon_1]+z\alpha n_0S_x/2}{kT}\right\},$$

and

$$Q''=\sum_{\substack{W=0\\ f,n_0}}^{W=1} W(f,n_0)\exp\left\{-\frac{[f(x-3)n_x\epsilon_2+(1-f)(x-3)n_x\epsilon_1]+z\alpha n_0S_x/2}{kT}\right\}.$$

Now, since Flory's[4] expression for W is essentially[14]

$$W=\frac{(xn_x+n_0)!\,z^{xn_x}\left\{\frac{[(z-2)x+2]n_x+zn_0}{2}\right\}!\,(z-1)^{n_x}(z-2)^{f(x-3)n_x}[(x-3)n_x]!}{(n_0)!\,[(xn_x+n_0)z/2]!\,2^{xn_x}(n_x)!\,[(1-f)(x-3)n_x]!\,[f(x-3)n_x]!}, \tag{5}$$

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[13] E. A. Guggenheim, Proc. Roy. Soc. (London) **A183**, 203 (1944–1945).

[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_1, of solvent molecules in place of our number, n_0, of holes; second, his expression is the result of use of the fraction $(N_0-xi)/N_0$ 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, $(N_0-x_i)/[N_0-2(x-1)i/z]$, 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' may be factored,

$$Q'=\left\{\sum_{n_0}\frac{(xn_x+n_0)!\,z^{xn_x}\left\{\dfrac{[(z-2)x+2]n_x+zn_0}{2}\right\}!\,(z-1)^{n_x}\exp\left(-\dfrac{z\alpha n_0 S_x}{2kT}\right)}{(n_0)!\,[(xn_x+n_0)z/2]!\,2^{xn_x}}\right\}$$

$$\times\left\{\sum_{f}\frac{(z-2)^{f(x-3)n_x}[(x-3)n_x]!\exp\left[\dfrac{-(1-f)(x-3)n_x\epsilon_1-f(x-3)n_x\epsilon_2}{kT}\right]}{[(1-f)(x-3)n_x]!\,[f(x-3)n_x]!\,(n_x)!}\right\}=\mu'\lambda', \quad (6)$$

where λ' represents the factor which is summed over f, and μ' the factor which is summed over n_0.

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

$$\lambda'=\frac{[\exp(-\epsilon_1/kT)+(z-2)\exp(-\epsilon_2/kT)]^{n_x}}{(n_x)!}. \quad (7)$$

For the "free energy" derived from λ', we have

$$F'_{\lambda'}=-kT\ln\lambda'. \quad (8)$$

We may now show that the maximum term of λ', $\lambda'_{\max}$, is an excellent representation of λ' itself. Differentiating the generic term of λ' and equating to zero we find

$$f'_{\max}=(z-2)\exp[-(\epsilon_2-\epsilon_1)/kT]/$$
$$1+(z-2)\exp[-(\epsilon_2-\epsilon_1)/kT] \quad (9)$$

for the most probable value of f obtained from Q'.

Substituting this expression for f in the generic term of λ' to get $\lambda'_{\max}$, forming $F'_{\lambda'\max}=-kT\ln(\lambda'_{\max})$ and comparing with $F'_{\lambda'}$ we see that

$$\lim_{n_x\to\infty}\left(\frac{F'_{\lambda'\max}-F'_{\lambda'}}{n_x}\right)=0. \quad (10)$$

A similar treatment of μ' is not possible since (1) the sum over n_0 is intractable and (2) the expression for $n'_{0\max}$, the most probable value of n_0 derived from Q', is transcendental and involves $n'_{0\max}$ only implicitly:

$$\ln(V_0^{z/2-1}/S_0^{z/2})-(z\alpha S_x^2/2kT)=0. \quad (11)$$

Nevertheless, it may be seen by numerical inspection that the term in μ' involving $n'_{0\max}$ makes the only significant contribution to μ' just as the term involving $f'_{\max}$ makes the principal contribution to λ'. Thus

$$\lim_{n_x\to\infty}\left(\frac{F'_{\mu'\max}-F'_{\mu'}}{n_x}\right)=0, \quad (12)$$

where the symbols $F'_{\mu'\max}$ and $F'_{\mu'}$ have a significance which is parallel to those of $F'_{\lambda'\max}$ and $F'_{\lambda'}$.

Furthermore,

$$\ln(Q'_{\max})=\ln(\lambda'_{\max}\mu'_{\max})\leq\ln Q\leq\ln Q', \quad (13)$$

and

$$\ln(Q_{\max})\leq\ln Q\leq\ln Q', \quad (14)$$

if the maximum term, $Q'_{\max}$, of Q' is also the maximum term, $Q_{\max}$, of Q, a condition which is true if the associated value of W in the former (i.e., $W'_{\max}$) is greater than unity, so that $Q'_{\max}$ does not appear in Q''. Therefore, we have

$$F_{\max}=-kT\ln(Q_{\max})\geq F=-kT\ln Q\geq F'$$
$$=-kT\ln Q' \quad (15)$$

as long as $W'_{\max}\geq 1$. Clearly then

$$\lim_{n_x\to\infty}\left(\frac{F-F'}{n_x}\right)=0,\quad \lim_{n_x\to\infty}\left(\frac{F_{\max}-F}{n_x}\right)=0, \quad (16)$$

so that F' and $F_{\max}$ are both valid expressions for the free energy when the maximum term of Q' is a term allowed in Q.

Since $W'_{\max}$ is a monotonically increasing function of T, we may say that these expressions for F are valid for all $T\geq T_2$, where T_2 indicates the point where $W'_{\max}=1$.

Henceforth we will replace the superscript, ′, and the combination of a superscript, ′, and a subscript, max, on the symbols representing expressions for thermodynamic variables with a subscript, $>T_2$, to indicate the region of validity of the corresponding expressions.

We have now obtained the results,

$$F_{>T_2}=-kT\ln Q'=-kT\ln Q'_{\max}$$

$$=-kTxn_x\left[\left(\frac{z-2}{2}\right)\ln\left(\frac{V_0}{S_0}\right)+\left(\frac{n_0}{xn_x}\right)\ln\left(\frac{V_0^{z/2-1}}{S_0^{z/2}}\right)+\frac{\ln\left\{\dfrac{[(z-2)x+2](z-1)}{2}\right\}}{x}\right.$$

$$\left.+\left(\frac{x-3}{x}\right)\ln[e^{-\epsilon_1/kT}+(z-2)e^{-\epsilon_2/kT}]-\frac{\alpha z n_0 S_x}{2kTxn_x}\right]. \quad (17)$$

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 $T \leq T_2$, of the term which is the maximum one at T_2 to any other allowed term,

$$r=\left(\frac{1}{W(f_1,n_{01})}\right)\frac{\exp[-E(f_{T_2},n_{0T_2})/kT]}{\exp[-E(f_1,n_{01})/kT]}\geq\left(\frac{1}{W(f_1,n_{01})}\right)\left(\frac{\exp[-E(f_{T_2},n_{0T_2})/kT]}{\exp[-E(f_1,n_{01})/kT]}\right)^{T/T_2}$$
$$=\frac{(1)\exp[-E(f_{T_2},n_{0T_2})/kT_2]}{W(f_1,n_{01})\exp[-E(f_1,n_{01})/kT_2]}>1, \quad (18)$$

since $W(f_1,n_{01})>1$ (allowed term). f_{T_2} and n_{0T_2} 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,

$$F_{<T_2}=-kT\ln[Q_{\max}(f_{T_2})]=\frac{z\alpha n_{0T_2}S_{xT_2}}{2}+f_{T_2}(x-3)n_x\epsilon_2+(1-f_{T_2})(x-3)n_x\epsilon_1. \quad (17A)$$

The two expressions, (17) and (17A), for the free energy are, of course, equal at T_2,

$$\lim_{T\to T_2}(F_{>T_2}(T))=\lim_{T\to T_2}(F_{<T_2}(T)). \quad (19)$$

For the entropy, S, we have

$$S_{>T_2}=-\frac{\partial F_{>T_2}}{\partial T}=kxn_x\left[\left(\frac{z-2}{2}\right)\ln\left(\frac{V_0}{S_0}\right)+\frac{n_0}{xn_x}\ln\left(\frac{V_0^{z/2-1}}{S_0^{z/2}}\right)+\frac{\ln\left\{\frac{[(z-2)x+2](z-1)}{2}\right\}}{x}\right.$$
$$\left.+\left(\frac{x-3}{x}\right)\left\{\ln[e^{-\epsilon_1/kT}+(z-2)e^{-\epsilon_2/kT}]+\frac{\left(\frac{\epsilon_1}{kT}\right)e^{-\epsilon_1/kT}+\left[\frac{(z-2)\epsilon_2}{kT}\right]e^{-\epsilon_2/kT}}{e^{-\epsilon_1/kT}+(z-2)e^{-\epsilon_2/kT}}\right\}\right], \quad (20)$$

$$S_{<T_2}=-\partial F_{<T_2}/\partial T=0, \quad (20A)$$

and

$$\lim_{T\to T_2}(S_{>T_2}(T))=\lim_{T\to T_2}(S_{<T_2}(T))=0. \quad (21)$$

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

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

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, α, 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

$$V_{>T_2}=C(T)[xn_x+n_0(T)], \quad (23)$$

$$V_{<T_2}=C(T)[xn_x+n_0(T_2)], \quad (23A)$$

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

$$\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_{>T_2}=\frac{\partial C/\partial T}{C}+\frac{\partial n_0/\partial T}{xn_x+n_0}=\frac{\left(\dfrac{z\alpha}{2kT^2}\right)V_0S_x^2}{zS_x/2-\dfrac{z\alpha S_0S_x^2}{kT}-(z/2-1)V_x}+\frac{\partial C/\partial T}{C}, \tag{24}$$

$$\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_{<T_2}=\frac{\partial C/\partial T}{C}. \tag{24A}$$

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 $f_{\max}$), and (2) the volume ($n_{0\max}$) 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 must 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_2, 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 $W_{\max}=1$ as the criterion for T_2, but use of reasonable (small compared to xn_x) values of the degeneracy of this ground state[15] 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_2 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 α and $(\epsilon_2-\epsilon_1)$ for

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[15] There are two possible types of ground-state degeneracy: the first arises from the possibility that the lowest values of f and n_0 which yield any mode of packing the chains on the lattice at all actually yield more than one mode; the second arises from some trivial characteristic (for example, location of nuclear isotopes) which distinguishes several configurations among one mode of packing. The second type is trivial because it affects higher energy levels and the ground level in the same way, and thus gives rise to only a temperature independent entropy of mixing and has no effect at all on the volume or energy. It may be neglected in the evaluation of $W(f,n_0)$, and therefore $S_{>T_G}$ if it is also neglected in the specification of the lower limit to W, andthere fore $S_{<T_G}$, 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

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

and Eq. (24). $(\epsilon_2-\epsilon_1)$ is easily obtained from Eq. (22) and the experimental value for the glass temperature.

If we wish to predict volume changes above T_G, we must also have information concerning C. Since

$$\lim_{T\to T_G}\left(\frac{\partial C/\partial T}{C}\right)=\lim_{T\to T_G}\left(\frac{\partial C/\partial T}{C}\right), \qquad (26)$$

we may expect that the expression, $\partial C/\partial T/C=\text{constant}$, which describes C well below T_G,[16] 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 ($x=1640$).

$$\lim_{\delta\to 0}\left[\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_{T_G+\delta}-\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_{T_G-\delta}\right]=2.9\times10^{-4}/{}^\circ\mathrm{K}. \qquad (27)$$

$$\left(\frac{1}{V}\frac{\partial V}{\partial T}\right)_{T<T_G}=2.2\times10^{-4}/{}^\circ\mathrm{K}.$$

$$T_G=373{}^\circ\mathrm{K}. \quad V_{T_G}=0.969\ \mathrm{ml/g}.$$

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

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

$$\frac{(\epsilon_2-\epsilon_1)}{k}=839.3{}^\circ\mathrm{K} \qquad (28)$$

$$xn_xC=0.86274\exp(2.2\times10^{-4}T)\ \mathrm{ml/g}.$$

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 α. 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 (determination of $\epsilon_2-\epsilon_1$ at $x=1640$, i.e., molecular weight of 85 000), we realize that the agreement displayed at low x is startling. Furthermore, the shape of this curve is quite insensitive to α as long as α is not absurdly low, so that an almost equally good fit to the experimental points can be obtained with any reasonable α on adjustment of the one parameter, $\epsilon_2-\epsilon_1$. In fact, fairly good agreement can even be obtained if holes are neglected entirely by use of infinite α. The value of α used in the curve shown was, of course, determined from the independent quantity expressed in Eq. (24), as already described.

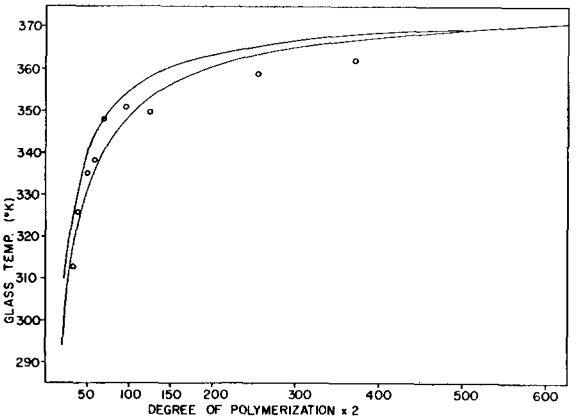

FIG. 1. Glass transition temperature of polystyrene as a function of molecular weight (in units of x). The upper theoretical curve was derived with use of the "Huggins fraction"[14] [and therefore Eq. (5)], the lower one with use of the "Flory fraction."[14] The circles are the experimental data of Fox and Flory.[17]

Now the values of $(\epsilon_2-\epsilon_1)$ must themselves obey certain criteria. They must, first of all, be reasonable in the light of studies of hindered internal rotation in simple molecules. Then too, they must be greater for chains which are known to be stiff than for chains which are known to be flexible from independent experiments such as light scattering investigations of mean square (end-to-end) lengths in solution. A survey of the literature for values of glass temperatures of polymers and calculation of the values of $(\epsilon_2-\epsilon_1)$ from these[18] shows that these conditions hold, apparently without exception. Sample values of $(\epsilon_2-\epsilon_1)$ are 1.44 [kcal/(mole of segments)] for polymethyl methacrylate, 1.43 for polystyrene, 1.16 for polyvinyl chloride, 1.15 for polyvinyl acetate, 0.97 for polyvinylidine chloride, and 0.76 for polyisobutylene. The pair, polyvinyl chloride and polyvinylidine chloride is interesting. The introduction of the second chlorine atom in the monomer unit of polyvinylidine chloride certainly raises the absolute values of the energies associated with all the various angles of rotation around a given chain bond (i.e., of both the potential energy minima and the potential energy barriers between minima), but at the

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[16] The equation, $\partial C/\partial T=\text{constant}$, works equally well.

[17] T. G. Fox and P. J. Flory, J. Appl. Phys. 21, 581 (1950); J. Polymer Sci. 14, 315 (1954).

[18] Since we are only concerned here with the approximate values of $\epsilon_2-\epsilon_1$ and their variation among the various polymers, and since T_G is relatively insensitive to α, we have used $\alpha=\infty$ in the calculation of these values of $\epsilon_2-\epsilon_1$ from T_G.

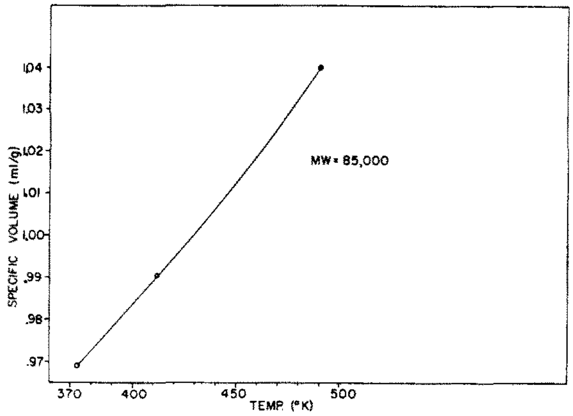

FIG. 2. Theoretical variation (the curve) of specific volume with temperature for polystyrene of molecular weight 85 000 and the experimental points (the three circles) of Fox and Flory.[17]

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[17,21] 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/xn_x with temperature. This strongly suggests that a straight line should not be used to represent the experimental data.[22]

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 polymer chains involved in the experimental study had end groups which were slightly different from the other segments. It should also be noted that the data of Ueberreiter and Kanig,[21] presented in Fig. 4, suggest somewhat lower values for the specific volumes at low molecular weights.

The upswing in specific volume at low molecular weights has generally been attributed to a difference between the length of a covalent bond and the length of a "van der Waals bond," since the process of chopping a polymer chain into two shorter chains involves the introduction of a "van der Waals bond" at the expense of a covalent bond. However, that degree of upswing which is exemplified by the theoretical curve in Fig. 3 is achieved without invocation of this effect.

The plot given in Fig. 4 of the specific volume at the glass temperature V_{T_G} *versus* the value of the glass temperature for different molecular weights of polystyrene is quite illuminating. The slope of the theoretical curve is not simply the expansion coefficient of polystyrene in the glassy state. Thus T_G, insofar as it can be identified with T_2, is not characterized by a particular value of the "free volume," n_0. The value of n_0 at and below T_G is greater for the polystyrene fractions with high molecular weight and, therefore, high T_G than it is for those of low molecular weight and low T_G.

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

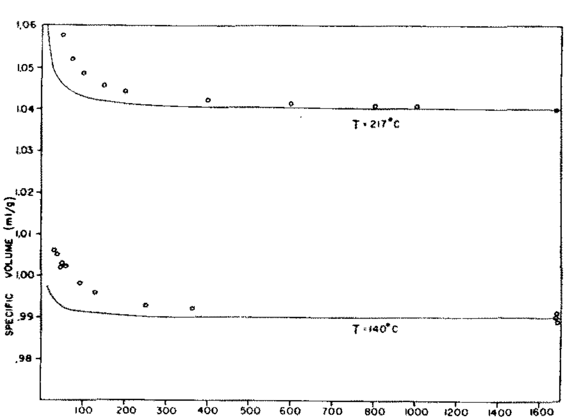

FIG. 3. Theoretical variation (the curves) of specific volume with molecular weight (in units of x) for two temperatures, 140°C and 217°C, and the corresponding experimental data (circles) of Fox and Flory. The upper circles were actually obtained from a curve which best fits the experimental data.

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[19] 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-(n-alkyl) methacrylates, for which light scattering studies indicate roughly equal chain stiffnesses.

[20] A collection of appropriate references is given in reference 19.

[21] K. Ueberreiter and G. Kanig, J. Colloid Sci. 7, 569 (1952).

[22] Fox and Flory[17] have suggested this on observation of their experimental data on polystyrene.

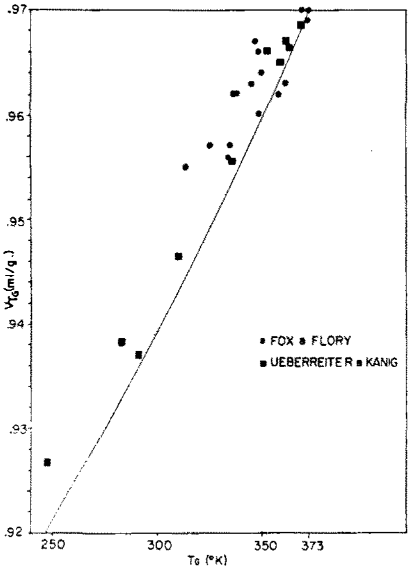

FIG. 4. The theoretical relation (the curve) between the specific volumes at their glass transition temperatures of polystyrene samples of varying molecular weight and the glass transition temperatures, compared with the corresponding experimental data of Fox and Flory,[17] and Ueberreiter and Kanig.[21]

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[23] and polyisobutylene.[24] 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, ϵ_2, may be used for them all affects adversely the quantitative agreement which may be obtained between theoretical and experimental results for this property.[25,26]

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 $(\epsilon_2-\epsilon_1)$ 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.[27]

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.[28] 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 ∞, to those of a monodisperse system of $n_{\bar{x}}$ $\bar{x}$-mers, the "number average" chain length, $\bar{x}$, being defined by

$$\bar{x}=\sum_{i=3}^{\infty} in_i/n_{\bar{x}}, \tag{29}$$

where

$$n_{\bar{x}}=\sum_{i=3}^{\infty} n_i. \tag{29A}$$

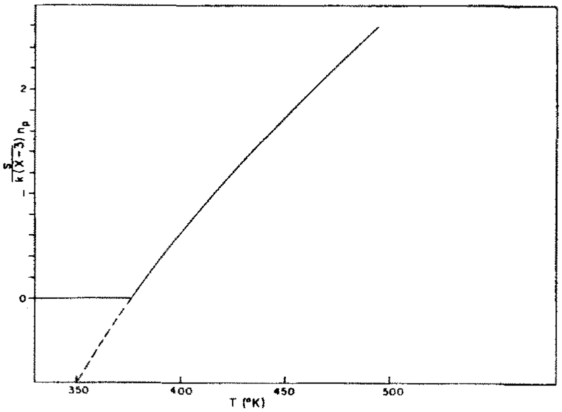

FIG. 5. Configurational entropy (of polystyrene of $x=\infty$) as a function of temperature.

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[23] K. Ueberreiter and S. Nens, Kolloid-Z. **123**, 94 (1951).

[24] G. T. Furukawa and M. L. Reilly, J. Research Natl. Bur. Standards **56**, 285 (1956).

[25] 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 $(\epsilon_2-\epsilon_1,)$ determined from the glass temperature, to give the correct value for the specific heat discontinuity.

[26] If the "potential energy well" whose bottom is ϵ_2 has a shape (force constant) different from that whose bottom is ϵ_1, 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.

[27] 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.

[28] 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

$$\begin{aligned} E &= f\sum_{i=3}^{\infty}(i-3)n_i\epsilon_2+(1-f)\sum_{i=3}^{\infty}(i-3)n_i\epsilon_1 \\ &= f(\bar{x}-3)n_{\bar{x}}\epsilon_2+(1-f)(\bar{x}-3)n_{\bar{x}}\epsilon_1, \end{aligned} \tag{30}$$

the intermolecular energy as

$$\Phi = z\alpha n_0 S_{\bar{x}}/2, \tag{31}$$

where

$$S_{\bar{x}}=\frac{\sum_i[(z-2)i+2]n_i}{\sum_i[(z-2)i+2]n_i+zn_0}=\frac{[(z-2)\bar{x}+2]n_{\bar{x}}}{[(z-2)\bar{x}+2]n_{\bar{x}}+zn_0},$$

and the number of configurations, $W(f,n_0\cdots n_i\cdots i\cdots)$ as[29]

$$W(f,n_0\cdots n_i\cdots i\cdots)=W(f,n_0,n_{\bar{x}},\bar{x})\cdot\frac{(n_{\bar{x}})!}{\prod_{i=3}^{\infty}(n_i)!}. \tag{32}$$

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[21] 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 $i\geq 3$ is the same as that of an equivalent number, $n_{\bar{x}}$, of dissolved $\bar{x}$-mers ($\bar{x}$ and $n_{\bar{x}}$ 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,[3,4] except for a factor $(n_1+n_0)!/(n_1)!(n_0)!$ 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[30] 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

$$\begin{aligned} 0=\bar{\bar{x}}n_{\bar{\bar{x}}}\Bigg[&\left(\frac{z-2}{2}\right)\ln(V_0/S_0)+\left(\frac{n_0}{\bar{\bar{x}}n_{\bar{\bar{x}}}}\right)\ln\left(\frac{{V_0}^{z/2-1}}{{S_0}^{z/2}}\right) \\ &+\frac{\ln\{[(z-2)\bar{\bar{x}}+2](z-1)/2\}}{\bar{\bar{x}}}\Bigg]+(\bar{x}-3)n_{\bar{x}} \\ &\times\{\ln[1+(z-2)e^{-(\epsilon_2-\epsilon_1)/kT}]+f(\epsilon_2-\epsilon_1)/kT\} \\ &+[n_{\bar{\bar{x}}}\ln(n_{\bar{\bar{x}}})-\sum_{i=2}^{\infty}n_i\ln n_i]-n_2\ln(z-1), \end{aligned} \tag{33}$$

where now

$$\bar{\bar{x}}=\sum_{i=2}^{\infty}in_i\Big/\sum_{i=2}^{\infty}n_i,$$

$$n_{\bar{\bar{x}}}=\sum_{i=2}^{\infty}n_i,$$

and

$$V_0=n_0/\bar{\bar{x}}n_{\bar{\bar{x}}}+n_0,\quad S_0=zn_0/[(z-2)\bar{\bar{x}}+2]n_{\bar{\bar{x}}}+zn_0.$$

In Fig. 6 we show, along with the experimental data, a plot of this theoretical result as a function of % monomer (styrene), $100\,(2n_2)/\bar{\bar{x}}n_{\bar{\bar{x}}}$, the values of $(\epsilon_2-\epsilon_1)$ and α being the same as before. The lower curve is the result obtained when holes are neglected entirely ($\alpha=\infty$). It may be seen that these curves afford a good representation of the experimental data.[31]

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, $f_{<T_G}$, is given by a formula identical to (9) except for the replacement of T with T_G,[32] $f_{<T_G}$ is dependent, through T_G, on the variables, such as percent monomer and chain length, which influence T_G. A similar statement may be made concerning the number of holes in the glassy state, n_{T_G}.

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[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 number of ways. Thus, this number of modes of packing depends on $\bar{x}$ and $n_{\bar{x}}$ in the case considered here in the same way as it depended on x and n_x 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).

[30] A. P. Alexandrov and J. S. Lazurkin, Compt. rend. acad. sci. U.R.S.S. **43**, 376 (1944).

[31] For monomer concentrations higher than 20%, the theoretical curve for which the effect of holes was considered behaves "badly". There are a number of reasonable explanations for this.

[32] The fact that this formula for $f_{<T_G}$ and formula (9) itself for $f_{>T_G}$ are still valid in this case of a solution may be recognized from the observation that the factor in the partition function which depends on chain stiffness (and, of course, the total number of segments) and from which the expression for $f_{<T_G}$ and $f_{>T_G}$ are derived is unchanged and still separable from the rest of the partition function at and above T_G.

Kargin[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_0, 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_0 with n_2, has been observed by Kovacs.[34]

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).[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 viscoelastic (and dielectric) sluggishness near T_2, which the present equilibrium theory affords, will lead to a quantitative (nonequilibrium) theory for this sluggishness in the near future.

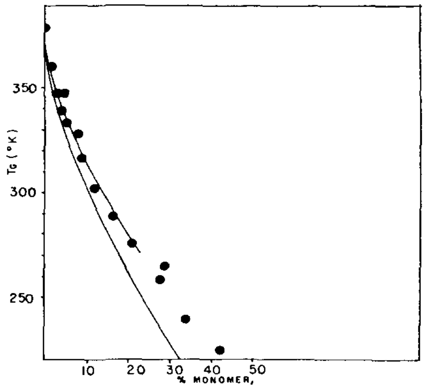

FIG. 6. The variation of glass transition temperature with solution composition for solutions of polystyrene in styrene monomer. The derivation of the upper theoretical curve allowed for the effect of "holes" whereas that of the lower one did not. The points are the data obtained experimentally by Alexandrov and Lazurkin.[30]

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 quasi-lattice 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.

ACKNOWLEDGMENT

We are very grateful to Dr. Frank Collins and Dr. Elio Passaglia for many helpful discussions. We also express our thanks to Miss Eleanor Houghton for the programming of certain machine computations and to Mr. Stanley Wojcicki, Mr. Max Cohen, and Mr. Aaron Gara for preliminary computations.

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[33] V. A. Kargin, J. Polymer Sci. **23**, 47 (1950).

[34] A. Kovacs, Compt. rend. **235**, 1127 (1952); **235**, 1648 (1952).

[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°C, but the latter is somewhat less successful.