The Role of Chain Conformation in the Theory of Glasses. 1. The Glass Transition

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ABSTRACT: A new approach is developed in this series to analyze the role of chain conformation in equilibrium thermodynamics and kinetics of the glass-transition phenomenon. In this paper, we focus our attention on the "equilibrium" glass-transition temperature (T_r) which is treated as a thermodynamic anomaly, not a second-order phase transition, by utilizing Flory's lattice statistics of chain molecules. T_r occurs when the most stable hole configuration is reached under the cooperative constraint of linear chains. The analysis reveals that (1) T_r is mainly determined by the stiffness of the polymeric chain, which is consistent with the conclusion of the Gibbs–DiMarzio theory, and that (2) the ratio of the hole (intermolecular) and flex (intramolecular) energies varies only between 2 and 2.3, which supports the notion that the conformational theory is experimentally equivalent to the hole theory. The ubiquitous nature of glass formation is also explained.

I. Introduction

Two different views have been adopted in the molecular interpretation of the glass transition and the glassy state of polymers. One view considers conditions when relaxation processes occur so slowly that the glass transition can be treated as a time-independent phenomenon. The other view is directed at the nonequilibrium character of structural relaxation and physical aging. The concept of free volume (holes) has been widely used in both approaches,[1-5] but the role of chain conformation, in spite of its importance, has not received the same amount of attention. The Gibbs–DiMarzio (GD) theory[6] is perhaps the most successful[7-10] equilibrium theory of glasses which takes into account both the conformational and hole energies. In the GD theory, a second-order phase transition in the Ehrenfest sense is identified with the glass transition, and the configurational entropy equals zero at the transition. An equilibrium theory should serve as the foundation onto which a nonequilibrium theory is built. The lack of progress in extending the GD theory from equilibrium to nonequilibrium may be related to the criticism that the second-order phase transition postulated in the theory has received.[11]

The purpose of this paper is to remove the second-order phase transition requirement in the GD theory but retain the essential features which make this theory successful. We shall treat the "equilibrium" glass temperature (T_r) as a thermodynamic anomaly rather than a phase transition. DiMarzio[12] has mentioned that the ubiquitous nature of glass formation must be explained even for nonpolymeric systems. The new T_r criterion proposed here will not fail in the same way as the condition of zero configuration entropy.[12,13] The Flory–Huggins lattice model, based on its successful application in polymer science, serves as the starting point in this paper. The result of our calculation will be compared with those published in the literature.

II. Equilibrium State

Consider a system consisting of n holes (free volume) and n_x linear polymer chains of x monomer segments each. The change from one conformation to another occurs as a result of internal rotations about single bonds. In order to see the effect of the rotamers (conformers), internal parameters have to be included in the analysis. In the simplest case, we assume that there are only two intramolecular energy levels, 0 and ϵ_f. The flex energy (ϵ_f) is assumed to be the conformational energy difference between high-energy gauche and low-energy trans states. Let f be the fraction of bonds in all the molecules with flex energy, ϵ_f. The total number of lattice sites is written in the form

$$N = n + xn_x[f + (1 - f)] \tag{1}$$

Each lattice site occupies a single lattice cell with volume

$$v = v_h + (1 - 2/x)fv_f \tag{2}$$

where the subscripts h and f refer to the hole and flex bond, respectively. In the spirit of the mean field approximation, the effect of internal rotations on the lattice volume is given by the second term in the above equation where $f(x - 2)n_x$ flex bonds are considered. The flex (conformational) volume (v_f) is much smaller than v_h. The total volume of the system is $V = vN$.

The number of ways that are allowed for the internal parameters n and f to be arranged in the system has been estimated by Flory's combinatorial statistics.[14] The total number of configurations is given by

$$W = {q_h}^n {q_x}^{xn_x} \frac{N! N^{-(x-1)n_x} z^{n_x} (z - 2)^{f(x-2)n_x}}{n! n_x! 2^{n_x}} \binom{(x - 2)n_x}{f(x - 2)n_x} \tag{3}$$

where z is the lattice coordination number and q_h and q_x are the internal configurations which contribute to the internal entropies associated with a hole, $S_h = k \ln q_h$, and a monomer $S_x = k \ln q_x$. Equation 3 is simpler than the modified Huggins' expression used in the GD theory. When the molecular weights are sufficiently large, which is an implicit assumption in Flory's statistics, we shall see that eq 3, without modification, is adequate in analyzing the glass-transition phenomenon.

Upon use of Sterling's approximation for factorials, the total configurational entropy of the system becomes

$$S = k \ln W = nS_h + xn_xS_x + S_{mix} \tag{4}$$

where k is the Boltzmann constant and the entropy of mixing

$$S_{mix}/k = -[n \ln h + n_x \ln (1 - h)] + n_x[\ln (xz/2) - (x - 1)] - (x - 2)n_x[f \ln f + (1 - f) \ln (1 - f) - f \ln (z - 2)] \tag{5}$$

is dominate over the xn_xS_x term. The total enthalpy due to the introduction of holes and flex bonds is

$$H = n(\epsilon_h + pv_h) + f(x - 2)n_x(\epsilon_f + pv_f) \tag{6}$$

It is a sum of the inter- and intra-molecular contributions in which p is the pressure. Although $v_f \ll v_h$, the above equation suggests that the effect of the flex volume introduced in eq 2 should be seen at high pressures, which is consistent with a reported observation.[15] This effect is,

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however, not included in the GD theory.

The excess Gibbs free energy of the system is

$$G = H - TS \tag{7}$$

The equilibrium values of n and f are determined, respectively, from the conditions

$$\partial G/\partial n = 0 \tag{8}$$

and

$$\partial G/\partial f = 0 \tag{9}$$

When eq 4–7 are substituted into eq 8 and 9, the equilibria $\bar{n}$ and $\bar{f}$ are obtained. The equilibrium free volume fraction ($\bar{h} = \bar{n}/\bar{N}$) is

$$\bar{h} = c \exp\left(-\frac{\epsilon_h + pv_h}{kT}\right) \tag{10}$$

where $c = \exp(S_h/k + 1/x - 1)$ and $\bar{N} = \bar{n} + xn_x$. The equilibrium fraction of flex bonds is

$$\bar{f} = \left[1 + \exp\left(\frac{\epsilon_f + pv_f - \mu}{kT}\right)\right]^{-1} \tag{11}$$

where the chemical potential $\mu = kT \ln (z - 2)$ is an adjusting parameter for a particular polymer. Equations 1, 10, and 11 reveal the important differences between holes and rotamers which need to be mentioned. The number of rotamers is conserved, but the number of holes is not. Holes are created by raising the temperature and are eliminated by lowering it. Differing from rotamers, holes are independent of chemical potential through the neighboring coordinate constraints.

III. Ehrenfest Relations

In connection with the concept of a second-order phase transition, one employs the Ehrenfest equation

$$\frac{dT}{dp} = \frac{\Delta\bar{\kappa}}{\Delta\bar{\alpha}} = \frac{T\bar{V}\Delta\bar{\alpha}}{\Delta\bar{C}_p} \tag{12}$$

In evaluating this equation, we only need to consider the configurational contribution to the specific heat, $\bar{C}_p$; isothermal compressibility, $\bar{\kappa}$; and thermal expansion coefficient, $\bar{\alpha}$. From eq 1 and 2, the total equilibrium volume of the system is

$$\bar{V} = \bar{v}\bar{N} = xn_xv_h + \bar{n}v_h + (1 - 2/x)xn_x\bar{f}v_f + ... \tag{13}$$

The total equilibrium thermal expansion is given by

$$\bar{\alpha} = \frac{1}{\bar{V}}\left(\frac{\partial \bar{V}}{\partial T}\right)_p = \frac{1}{\bar{v}\bar{N}}\left[\bar{N}\left(\frac{\partial \bar{v}}{\partial T}\right)_p + \bar{v}\left(\frac{\partial \bar{N}}{\partial T}\right)_p\right] = \frac{1}{\bar{v}}\left(\frac{\partial \bar{v}}{\partial T}\right)_p + \frac{1}{\bar{N}}\left(\frac{\partial \bar{n}}{\partial T}\right)_p + (1 - 2/x)\frac{v_f}{\bar{v}}\left(\frac{\partial \bar{f}}{\partial T}\right)_p \tag{14}$$

The first term defines the lattice thermal expansion coefficient α_0 and has nothing to do with the transition phenomenon. The configurational thermal expansion coefficient is due to the second and third terms, which can be written more explicitly as

$$\Delta\bar{\alpha} = \bar{\alpha} - \alpha_0 = \left[y\bar{h} + \left(1 - \frac{2}{x}\right)\frac{v_f}{\bar{v}}\eta\bar{f}(1 - \bar{f})\right]\Big/ T \tag{15}$$

where the nondimensional parameters are

$$y = \frac{\epsilon_h + pv_h}{kT} \qquad \eta = \frac{\epsilon_f + pv_f}{kT} \tag{16}$$

In the same way, the configurational isothermal compressibility is

$$\Delta\bar{\kappa} = \left[v_h\bar{h} + \left(1 - \frac{2}{x}\right)\frac{{v_f}^2}{\bar{v}}\bar{f}(1 - \bar{f})\right]\Big/ kT \tag{17}$$

The configurational specific heat is

$$\Delta\bar{C}_p = \left(\frac{\partial \bar{H}}{\partial T}\right)_p = k\bar{N}\left[y^2\bar{h} + \left(1 - \frac{2}{x}\right)(1 - \bar{h})\eta^2\bar{f}(1 - \bar{f})\right] \tag{18}$$

Using eq 13, 15, 17, and 18, we find that the ratio

$$\frac{T\bar{V}(\Delta\bar{\alpha})^2}{(\Delta\bar{C}_p)(\Delta\bar{\kappa})} < 1 \tag{19}$$

is valid for all temperatures as long as $v_f/v_h \ll \epsilon_f/2\epsilon_h$, which is always true, as we shall see later. The above equation does not fulfill Ehrenfest's relation, eq 12, for the second-order phase transformation. Data near T_r on polymers usually support eq 19. Hence, T_r is not a phase transition.

IV. Thermodynamic Anomaly

The glass transition is a cooperative phenomenon. The conformational state of a given bond of a polymer chain depends on the conformational states of adjacent bonds.[16] The conformational interaction of two neighboring links has served as the basis of Flory's lattice statistics and of Birshtein and Ptitsyn's one-dimensional Ising model for a linear macromolecule. In fact, we shall find that both approaches result in the same anomalous temperature in the case of a linear polymer chain (see eq 22 below). Therefore, it is appropriate for us to consider linear macromolecules as one-dimensional Ising chains. This is one of the few cases that a one-dimensional Ising model can provide a good physical insight. The equilibrium specific heat of an Ising chain has no sharp transition but exhibits a broad and smooth maximum determined by[17]

$$\partial\Delta\bar{C}_p/\partial T = 0 \tag{20}$$

From the viewpoint of a relaxation process, what we have just discussed is the limiting case of a system being cooled or heated through T_r at the extremely slow rate (q). The relaxation time (τ) of polymers is a finite quantity. Therefore, the molecules of the system have sufficient time ($\tau \ll 1/q$ with $q \rightarrow 0$) to rearrange which means that $\Delta\bar{C}_p$ changes gradually with temperature and does not have a sharp peak of second-order phase transitions.

Substituting eq 18 into eq 20, we obtain

$$y^2(y - 2)\bar{h} + (1 - 2/x)(1 - \bar{h})\bar{f}(1 - \bar{f})[\eta(1 - 2\bar{f}) - 2] = 0 \tag{21}$$

In the case of $\bar{h} = 0$ and $p = 0$, the above equation reduces to

$$\frac{\epsilon_f}{2kT_r} \tanh\left(\frac{\epsilon_f - \mu}{2kT_r}\right) = 1 \tag{22}$$

When we further assume the chemical potential to be zero, eq 22 agrees exactly with the solution obtained from the matrix method calculation of the one-dimensional Ising problem.[16,17] The anomaly temperature is related to the flex energy by

$$\frac{\epsilon_f}{kT_r} = 2.4 \tag{23}$$

Equation 20 is basically the thermodynamic anomaly condition of a single chain in which only the intramolecular interaction is considered as an order parameter. The total polymeric system also includes the effect of intermolecular interaction which is characterized by the hole energy in

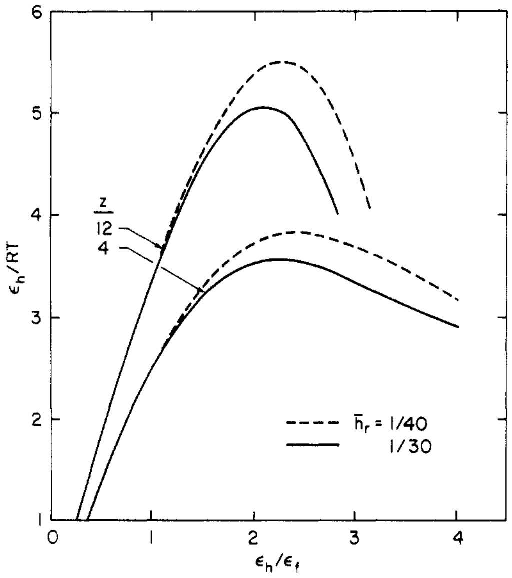

Figure 1. Maxima of the curves defining the equilibrium glass-transition temperature, T_r.

our model. Thus, another condition is needed which will specify the role of hole energy at T_r.

The glassy state has been treated as a state of frozen configurational disorder in our hole theory.[5] The notion is extended here by considering T_r as the equilibrium freezing temperature occurring when the most stable hole configuration is reached. Of course, the configurational disorder also includes the internal contribution from conformers at the present time. The most stable hole configuration corresponds to a close packing structure. The increase of the hole (intermolecular) energy favors close packing. On the other hand, the close packing becomes more difficult when the chain flexibility is decreased as the result of an increase in the flex energy. For quantitative estimation, we introduce the ratio of the hole and flex energies as an independent variable. In addition to eq 20, we require the nondimensional hole energy, y, to satisfy

$$\partial y/\partial(\epsilon_h/\epsilon_f) = 0 \qquad \text{at } T = T_r \tag{24}$$

as the thermodynamic anomaly conditions. The parameter y takes into account the energy of thermal motion and determines the equilibrium state of holes.

There is no simple analytical solution for eq 21 and 24. For the sake of simplicity in calculation, we assume $p = 0$ and $2/x \ll 1$, which is in the range of practical interest for most polymers. The free volume fraction at the glass temperature, $\bar{h}_r$, is usually between 1/40 and 1/30. The values of coordination number z vary from 4 to 12. The curves in Figure 1 are calculated from eq 21, and their maxima, which satisfy eq 24, define T_r. In Figure 2, we see the overall variations for ϵ_h/kT_r, ϵ_f/kT_r, and other pertinent parameters. In the GD theory, it has been mentioned that the hole and flex energies may not be independent.[8] When $z = 4$, the ratio, ϵ_h/ϵ_f, is found to be a constant.[7] Figure 2 reveals that the ratio of hole and flex energies, although not constant, varies only between 2 and 2.3 for polymers with different chemical potentials. This supports the notion that the conformational theory is experimentally equivalent to the hole theory for the molecular interpretation of T_r.

The hole energy has been determined from the equation of state calculation[18] for polymeric liquids and glasses. Upon using these predetermined hole energies and T_r of some linear amorphous polymers, the flex energies and their ratios are determined in Table I from Figure 2. The flex energies calculated from our model are compared with those[7,9] acquired from the GD theory and the direct conformational estimation[19] in Table II. They are in good agreement. From the figures and tables, one may choose $\bar{h}_r = 1/30$ and $z = 6$, which gives

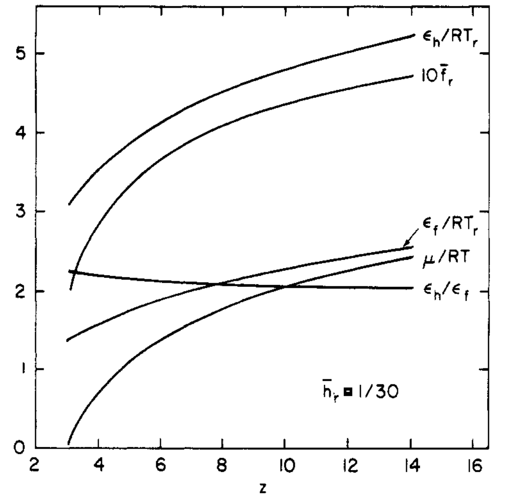

Figure 2. Relationship between the hole and flex energies and the chemical potential (or the lattice coordination number).

Table I
Estimation of the Flex Energies and Their Ratios from Predetermined Hole Energies[18] of Poly(vinyl acetate) (PVAc), Poly(vinyl chloride) (PVC), and Polystyrene (PS)

	PVAc	PVC	PS
T_r, K	308	360	371
ϵ_h, kcal/mol	2.51	2.92	3.58
ϵ_h/kT_r	4.11	4.09	4.86
ϵ_f/kT_r	1.90	1.88	2.36
ϵ_h/ϵ_f	2.16	2.18	2.06
ϵ_f, kcal/mol	1.16	1.34	1.74

Table II
Comparison of the Flex Energies Obtained from the Present Model and the GD Theory

	PVAc	PVC	PS
$T_r \simeq T_g$, K	305	350	373
(ϵ_f/k), K			
Eisenberg–Saito[7]	683	795	839
Havlicek et al.[9]	694	751	907
O'Reilly[19]	683	595	842
from Table I	584	675	877

$$\frac{\epsilon_h}{kT_r} = \frac{2.15\epsilon_f}{kT_r} = 4.16 \tag{25}$$

as a crude approximation for picturing the role of chain conformation in the glass transition.

The $S = 0$ theory concentrates entirely on barriers to rotation and is not applicable to nonpolymeric systems, which also form glasses. This is the case for $\bar{f} = 0$; eq 21, on the other hand, does not break down and becomes

$$\frac{\epsilon_h}{kT_r} = 2 \tag{26}$$

which is found applicable to inorganic glasses, such as As_2O_3 and B_2O_3. When eq 26 is used in the equation of state calculation, ϵ_h, T_r and $\bar{h}_r$ can be determined. The glass-transition temperature and hole energy are 433 K and 1.72 kcal/mol, respectfully, for Al_2O_3[20] and 530 K and 2.1 kcal/mol for B_2O_3.[21] The value for $\bar{h}_r$ is around 0.04, which is somewhat higher than the usual values for amorphous polymers.

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Finally, comparing eq 23, 25, and 26 reveals that the equilibrium glass-transition temperature, T_r, is mainly determined by the stiffness of the polymeric chain, which is consistent with the conclusion of the GD theory. The combination of eq 25 and 15, where the first term dominates, gives

$$\Delta\bar{\alpha} T_r \simeq \frac{\epsilon_h}{kT_r}\bar{h}_r = 0.139 \qquad (27)$$

which has the form of the Simha–Boyer equation.[2,8]

V. Conclusions

We have replaced the idea of the second-order phase transformation in the Ehrenfest sense postulated by the GD theory, yet retained its successful features in our new approach to T_r. The original Flory lattice model is used as the starting point in our analysis. The "equilibrium" freezing temperature is treated as the thermodynamic anomaly at which the most stable hole configuration is reached under the cooperative constraint of linear chain molecules. The results of our calculation compare well with the molecular parameters of polymers obtained from the GD theory by many other authors. The ubiquitous nature of the glass formation has been explained by our model even for nonpolymeric systems, while the $S = 0$ theory breaks down. The spin-related Ising anomaly and the free volume originated Simha–Boyer expression are among the special cases of the present interpretation. The equilibrium theory reported here serves as the foundation from which the role of chain conformation in kinetics will be discussed in the following paper in this issue.

Registry No. PVAc, 9003-20-7; PVC, 9002-86-2; PS, 9003-53-6.

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The Role of Chain Conformation in the Theory of Glasses. 2. Enthalpy Relaxation

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ABSTRACT: We have incorporated the role of the conformational energies of polymer chains in the kinetic theory of glasses by extending the equilibrium analysis developed in the first paper of this series. Under the cooperative constraints of hole distributions, a large number of conformational energy states are also introduced for the purpose of analyzing the nonequilibrium behavior. The departures from equilibrium for holes and flex bonds are then treated as a non-Markovian stochastic process. The theory shows how the kinetics of holes and bond rotations affect the enthalpy relaxation. The calculation reveals that the conformational activation energy is between 1 and 2 orders of magntiude lower than the hole activation energy. As a result, the enthalpy relaxes much faster than the volume at short times but approaches the same relaxation rate of volume at long times.

I. Introduction

There has been considerable interest in the structure relaxation and physical aging of glass-forming systems in recent years.[1-4] Free volume has played a central role in the molecular interpretation of the glass transition and the glassy state of polymers.[5-10] The concept has been generalized quite successfully in describing the volume relaxation and recovery processes. However, in the first paper[11] (which will be denoted as 1) of this series, we have seen that free volume alone cannot provide an adequate description of the glass temperature and enthalpy behavior of polymers. The role of chain conformation must enter the physical picture in order to gain a molecular understanding of the enthalpy relaxation in polymers. There is very little theoretical development in this area.

The purpose of this paper is to incorporate the effect of chain conformation in the kinetic theory of glasses by extending the equilibrium consideration developed in 1. In our earlier studies,[10] the kinetics of free volume over the glass-transition region is found as a result of the collapse of a series of free volumes having different levels of energies of hole formation. Its mean value determines thermodynamic equilibrium and intermolecular interaction and is equal to the hole energy used in 1. The same idea will be extended to the conformational energy. The conformational kinetics will be treated as a series of relaxational processes governed by a nonequilibrium transition-state theory. Both the volume and enthalpy relaxations will be calculated and compared. The success and the limitation of the free volume concept will be discussed.

II. Internal States

As mentioned in 1, we consider a system of n holes (or free volumes) and n_x polymer molecules of x monomer

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