Statistical mechanical theories of the glass transition — a new perspective

R. P. Kusy and A. R. Greenberg
Dental Research Center, University of North Carolina, Chapel Hill, NC 27514, *USA*
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The statistical mechanical functions of Gibbs and DiMarzio are briefly reviewed, and subsequent modifications of these equations by other workers are described. Then using computer analysis, three-dimensional representations of the two original expressions are developed to illustrate the overall multifunctional dependence. By recognizing that the free volume (V_0) is of secondary importance but that the ratio of the dimensionless parameter ($\beta = -\epsilon/kT_g$) is crucial, a reduced variables plot of $T_g/T_{g\infty}$ *versus* $10^3/\bar{P}$ is introduced. From a representative data sampling, the applicability of a single curvilinear function is established along with some initial observations.

Keywords Statistics; glass transition; mechanical theory; computer analysis; polymerization

INTRODUCTION

The relationship between glass transition temperature (T_g) and molecular weight has been extensively discussed in the polymer literature for over thirty years. In a recent publication on the glass transition of acrylic blends[1], the results indicated that the statistical theories of Gibbs and DiMarzio were superior to the free volume theory of Fox and Flory. This conclusion was not without some reservations, however, and a re-examination of both the Gibbs (G)[2] and Gibbs–DiMarzio (G–DM)[3] relationships was warranted. These rather cumbersome transcendental expressions can be restated for polydisperse systems as follows:

$$\text{G: } \frac{2\beta\exp\beta}{1+2\exp\beta} - \ln(1+2\exp\beta) = -\frac{\bar{x}}{\bar{x}-2}\left(\frac{V_0\ln V_0}{1-V_0} - \frac{\ln(2\bar{x})}{\bar{x}-2} + \frac{\bar{x}-1}{\bar{x}-2}\right) \tag{1}$$

$$\text{G–DM: } \frac{2\beta\exp\beta}{1+2\exp\beta} - \ln(1+2\exp\beta) = +\frac{\bar{x}}{\bar{x}-3}\left\{\frac{1}{1-V_0}\left[\ln V_0 + (1+V_0)\ln\left(\frac{(\bar{x}+1)}{2\bar{x}}\frac{1-V_0}{V_0}+1\right)\right] + \frac{\ln[3(\bar{x}+1)]}{\bar{x}}\right\} \tag{2}$$

where V_0 is the fractional free volume at T_g, k is Boltzmann's constant, ε is the energy difference between the favoured and the mean of the alternative chain conformations, $\bar{x}$ is the number average of chain atom segments (in this work restricted to equal the number average of chain backbone atoms), and β is a dimensionless parameter equal to $-\varepsilon/kT_g$.

In this paper a method of greatly simplifying equations 1 and 2 is introduced. Based upon a reduced plot of T_g against the reciprocal number average degree of polymerization ($\bar{P}^{-1}$), a single curve is generated for each theory which is applicable to all polymers. Prior to developing this new approach, however, certain problems associated with the use of the statistical mechanical theories must be resolved.

REVIEW OF THE LITERATURE

Besides the loss of signs (e.g., equation 10, ref. 4 and equation 3, ref. 5), misplacement of ln operations (e.g., equation 5, ref. 6), and absence of clarifying parentheses (e.g., equation 10, ref. 4 and especially equation 3, ref. 7), two particular assumptions have caused subsequent confusion. Both are related to the expression stated as equation 11 by Beevers and White over 20 years ago[4], i.e.:

$$\frac{2\beta\exp\beta}{1+2\exp\beta} - \ln(1+2\exp\beta) = -\frac{\bar{P}}{\bar{P}-2}\left(\frac{V_0\ln V_0}{1-V_0} - \frac{\ln 2\bar{P}}{\bar{P}} + \frac{\bar{P}-1}{\bar{P}}\right) \tag{3}$$

Comparison of the right hand sides of equations 1 and 3 shows that $\bar{P}$ had been substituted for $\bar{x}$ and that $\bar{P}-2$ had been approximated by $\bar{P}$ in the denominators of two bracketed terms. Each of these points is considered in turn.

In his pioneering work Gibbs used the Flory–Huggins lattice model and denoted the number of mers or monomer segments in the system as x (i.e., $\bar{x}$ in equation 1)[2]. In a later work with DiMarzio, Gibbs defined a monomer segment as the unit which occupied one lattice site—usually one main chain backbone atom plus attendant smaller side groups[3]. From this definition, the relationship between the number of backbone segments and the degree of polymerization could be stated as $\bar{x} = n\bar{P}$; where for vinyl polymers, $n=2$. In 1959, Beevers and White adopted the relationship $\bar{x} = \bar{P}$, presumably to obtain a better fit of their acrylic polymer data to the G equation[4]. While this form of equation 1 has proved useful over the years[1,5], its semi-empirical origins should be distinguished from the original theory. As indicated in *Figure 1*, substitution of $\bar{P}$ for $\bar{x}$ significantly decreases the predicted values of T_g, thereby shifting curve 1 to 1a.

Although an approximation such as $\bar{P}-2 \approx \bar{P}$ is

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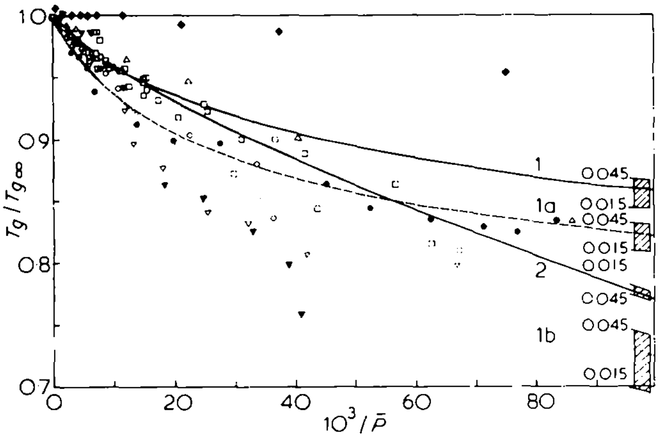

Figure 1 Reduced variables plot of the glass transition (T_g) as a function of the reciprocal degree of polymerization ($\bar{P}^{-1}$): ○, Beevers and White[4] on PMMA; ●, Kusy *et al.*[5] on PMMA; △, Ueberreiter and Kanig[11] on PS; □, Pezzin *et al.*[8] on PVC; ▽, Cowie and Toporowski[6] on PαMS; ▼, Malhotra *et al.*[11] on PαMS; and ◆, Cowie and McEwen[9] on PDMS. For $V_0 = 0.030$ curves 1, 1a, 1b, and 2 represent the Gibbs theory with $\bar{x} = 2\bar{P}$ (equation 1), the Gibbs expression used by Beevers and White[4] with $x = \bar{P}$ (equation 1), an erroneous interpretation of the Gibbs expression (equation 3), and the Gibbs–DiMarzio theory with $\bar{x} = 2\bar{P}$ (equation 2), respectively. Error bars for a given change in V_0 are indicated by the hatched regions to the right of each curve. These functions apply for constant ε

often implemented for high molecular weight polymers, a stepwise computer evaluation of each term of both functions shows that this assumption leads to erroneous conclusions. The adverse effects of this simple alteration of the G theory are all too clear when the modified expression is compared with the conventional formula (cf *Figure 1*, curves 1b and 1, respectively). Unfortunately this approximation was employed in subsequent studies of poly-α-methyl styrene (equation 6 of ref. 6) and polypropylene (equation 4 of ref. 7), thereby invalidating the conclusions derived from curve 2 in the first figure of both references. Ironically since Beevers and White used the original G formula with $\bar{x} = \bar{P}$ and not their equation 11 to plot curve 3 in *Figure 3* of ref. 4 correctly, this apparent simplification was not intentional.

PRELIMINARY OBSERVATIONS

From over forty sets of data compiled to date, selected results of five polymers were chosen for this study[4–6,8,9,11]: three vinyl polymers, polymethyl methacrylate (PMMA)[4,5], polystyrene (PS)[10], and polyvinylchloride (PVC)[8]; a divinyl polymer, poly-α-methyl styrene (PαMS)[6,11]; and a silicone elastomer, polydimethylsiloxane (PDMS)[9]. With respect to T_g *versus* $\bar{P}$ measurements, the first group represents the polymers of intermediate chain stiffnesses which have been most extensively researched. The other two reflect the extremes of polymer chain stiffnesses, ranging from a rigid polymer containing tertiary carbon atoms (PαMS) to a flexible one having ether linkages (PDMS).

These five polymers and the theoretical lines for the G (curves 1, 1a, and 1b) and the G–DM (curve 2) functions are plotted on a reduced plot of T_g *versus* $\bar{P}^{-1}$ for $V_0 = 0.030$ (cf *Figure 1*). Setting $\bar{x} = 2\bar{P}$, the results show that the PS[3] and PVC[8] data could be best approximated by the G–DM equation (curve 2). When this restriction is lifted, however, the G theory of Beevers and White is generally acknowledged to fit PMMA best (curve 1a)[4,5]. Note that within the limitations of the present formulae, no fit exists for either PαMS (▼ and ▽) or PDMS (◆). Hence the successful application of these theories to all polymers will require modification of the respective formulae to account for differences in chemical structure.

SPECIFIC THEORETICAL CONSIDERATIONS

Prompted by the computational difficulties noted previously, the immediate objective was not merely to improve but essentially to eliminate future calculations by designing a curve or a series of curves upon which data could be superposed and the quality of the fit assessed *via* statistical methods. Using a Wang 2200 PCS II computer, the first step was to generate the overall functional form of both theories. *Figure 2* shows both the G (left hand frame) and the G–DM (right hand frame) equations as a continuous function of $\bar{P}$, ε, and T_g for two discrete values of V_0, 0.015 and 0.045. From surfaces such as these, a volume is defined in which the molecular weight dependence of the second-order transition can be predicted for all polymers. Both of these plots demonstrate that most of the variation in T_g is dependent upon ε and not V_0 for the G–DM and to a lesser extent for the G theory. And although the sense of the ε – T_g slope (∝β) is the same for both expressions, the absolute magnitude of the slopes differ by about two-fold. The other significant difference between the two theories is the increased relative curvature of the G over the G–DM function.

The use of $\bar{P}$ rather than molecular weight places all polymers on the same basis so that only one three-dimensional solid is required for each theory. When a series of plots is made of T_g *versus* $10^3/\bar{P}$ for various ε's at constant V_0, a family of curves results which, from one plot to another, differ by only a shift factor. Adopting a procedure alluded to in a previous study[5], normalized rather than absolute T_g's were plotted, thereby collapsing the family of curves to a single line. Within this context, the lines shown in *Figure 1* are more than the single value solution that they appeared to be at the outset—curves 1 and 2 are the solution set for any value of ε ($\bar{x} = 2\bar{P}$).

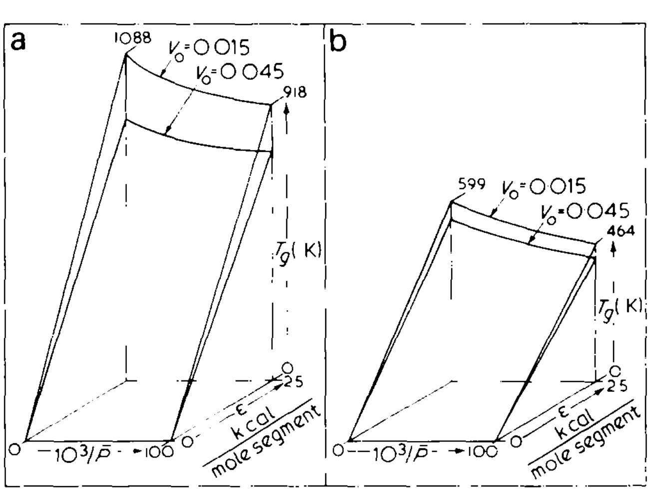

Figure 2 Overall functional appearance of the (a) Gibbs (equation 1) and (b) Gibbs–DiMarzio (equation 2) theories for $\bar{x} = 2\bar{P}$. Both ε and V_0 values were selected to encompass the current literature, whereas the degree of polymerization was limited by the relative increase in end group and side group activity

Table 1 Comparative parametric analyses of Gibbs–DiMarzio and Gibbs theories ($\bar{x} = 2\bar{P}$)

$10^3/\bar{P}$	V_0	$-\beta$	T_r*
0	0.015	2.092†; 1.152‡	1.000†; 1.000‡
	0.025	2.173; 1.260	
	0.035	2.244; 1.351	
	0.045	2.309; 1.430	
10	0.015	2.176; 1.209	0.961; 0.960
	0.025	2.260; 1.315	
	0.035	2.333; 1.405	
	0.045	2.400; 1.484	
20	0.015	2.243; 1.243	0.933; 0.937
	0.025	2.329; 1.349	
	0.035	2.405; 1.438	
	0.045	2.474; 1.517	
30	0.015	2.303; 1.269	0.908; 0.920
	0.025	2.392; 1.374	
	0.035	2.471; 1.463	
	0.045	2.543; 1.542	
40	0.015	2.362; 1.290	0.885; 0.907
	0.025	2.453; 1.395	
	0.035	2.535; 1.485	
	0.045	2.609; 1.564	
50	0.015	2.418; 1.307	0.864; 0.895
	0.025	2.513; 1.413	
	0.035	2.597; 1.503	
	0.045	2.675; 1.583	
60	0.015	2.474; 1.322	0.844; 0.886
	0.025	2.572; 1.428	
	0.035	2.660; 1.519	
	0.045	2.741; 1.599	
70	0.015	2.530; 1.335	0.825; 0.878
	0.025	2.632; 1.442	
	0.035	2.723; 1.533	
	0.045	2.807; 1.614	
80	0.015	2.586; 1.346	0.806; 0.870
	0.025	2.692; 1.454	
	0.035	2.787; 1.546	
	0.045	2.875; 1.627	
90	0.015	2.643; 1.356	0.788; 0.864
	0.025	2.753; 1.465	
	0.035	2.852; 1.557	
	0.045	2.945; 1.639	
100	0.015	2.701; 1.365	0.770; 0.858
	0.025	2.815; 1.474	
	0.035	2.919; 1.568	
	0.045	3.017; 1.651	

* Reduced glass transition temperature, $T_r = (T_g/T_{g\infty})$ at $V_0 = 0.030$
† Based on Gibbs–DiMarzio equation
‡ Based on Gibbs equation

To derive this conclusion, consider any polymer having a series of samples with different $\bar{P}^i$ where $i = 1, 2, \ldots j$. For a given free volume, V_0^i, a unique β^i will result, which is proportional to ε^i/T_g^i. If among all the samples chosen $\bar{P}^j$ is arbitrarily assigned to the sample with the highest molecular weight, then:

$$T_g^j \approx T_{g\infty} \propto \varepsilon^j/\beta^j \tag{4}$$

Since by definition the reduced parameter, $T_r^i = T_g^i/T_{g\infty}$, then:

$$T_r^i = \frac{\varepsilon^i}{\varepsilon^j} \times \frac{\beta^j}{\beta^i} \tag{5}$$

Finally because (under present constraints) for any particular polymer $\varepsilon^1 = \varepsilon^2 = \ldots \varepsilon^j$ over the range of $\bar{P}^i$:

$$T_r^i = \beta^j/\beta^i \tag{6}$$

DISCUSSION

As a result of equation 6, *Table 1* was derived to compare the influence of three absolute parameters $\bar{P}$, V_0, and β on T_r. In computing $10^3/\bar{P}$ from $\bar{P} = 10$ to ∞ and from $V_0 = 0.015$ to 0.045, the absolute value of β can be seen to vary. When each β is normalized, however, the T_r^i (or simply, T_r) values collapse so that to a first approximation the G and G–DM theories can be regarded as independent of V_0. On this basis both Fox and Flory's[12] increase in free volume associated with chain ends for $\bar{P} \gtrsim 300$ and Ferry's[13] constancy of free volume for a wide range of polymers can be placed in proper perspective. Consequently curves 1 and 2 graphically represent the reduced variable data of *Table 1*, column 4 for the G and G–DM equations for all polymers with a constant value of ε when $V_0 = 0.030$. The hatched areas to the right of these curves represent the maximum error bands found if V_0 were varied from 0.015 to 0.045 over the range $10^3/\bar{P} = 0$ to 100; these correspond to ~ 2 and 1% for the G and the G–DM theories, respectively. Finally note that while, for a given $\bar{P}$ and ε, the absolute value of T_g is inversely proportional to the number of holes, the reduced G and G–DM plots have opposite intraband trends (cf *Figure 1*). This inversion is caused by the greater negative slope of the T_g *versus* $10^3/\bar{P}$ plot for $V_0 = 0.015$ *versus* 0.045 (ε = constant; cf. *Figure 2a*).

The foregoing analysis greatly enhances the utility of the G and G–DM expressions. Whereas before each data set was first plotted and then fitted against one of the statistical mechanical functions after assuming a set of parameters, ε and V_0, now only one G or G–DM expression is needed for $\bar{x} = 2\bar{P}$. Consequently any further sets of data can simply be compared to the G or G–DM lines of *Figure 1*, curves 1 and 2, respectively. Within this context, a solution may exist for the vinyl polymer data specified herein; but no solution could exist for either PαMS or PDMS. With the restatement of these functions, the clarification of the previous literature, and the introduction of the reduced parameter plot, a more detailed analysis of the statistical mechanical approach can be considered for the general case of $\bar{x} = n\bar{P}$.

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