

Modification of the Adam–Gibbs Model of Glass Transition for Consistency with Experimental Data

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Received: February 17, 1999; In Final Form: May 17, 1999

We show that the Adam and Gibbs model of relaxation of liquid and polymeric glass-formers based on the configurational entropy, S_c , cannot account for several important experimental facts and phenomenology. These shortcomings include the decrease of the glass temperature when the glass-former is confined in nanometer pores, thermorheological complex nature of the viscoelastic spectrum of polymers, and also the deviation from a linear relation between $\log(\text{relaxation time})$ and $(TS_c)^{-1}$ found generally in fragile liquids. A closer reexamination of the Adam and Gibbs model indicates that the proposed transition rate of the cooperative rearranging regions does not seem to have captured all the complexities of molecular motion, i.e., their many-body dynamics. This aspect of the Adam–Gibbs model is improved by combining it with the coupling model to construct a modified model. The results of the modified model have the benefit of being consistent with all the experimental data considered.

1. Introduction

The connection between entropy and glass transition was first proposed by J. H. Gibbs¹ in 1956 to explain the “entropy crisis” noted by Kauzmann;² i.e., the difference in configurational entropy between the supercooled liquid and crystal seems to disappear at a finite temperature in the limit of infinitely slow cooling. The theory was developed in two subsequent papers. The first by Gibbs and DiMarzio³ in 1958 views the experimental glass transition as a signature of an underlying thermodynamics phase transition. The second by Adam and Gibbs⁴ (AG) in 1965 gives an expression for the relaxation time that contains the excess configurational entropy, S_c , of the Kauzmann paradox in the denominator of an exponent. Intuitively, in view of the entropy crisis, i.e., a decrease of S_c with decreasing temperature, thermodynamically the rearrangements over energy barriers of molecular units must be cooperative and further the size (defined by z^* , the number of molecular units) of the cooperating regions would necessarily increase with decreasing temperature. In arriving at the well-known result, AG made several assumptions. The first one is that the transitions of the cooperative regions involve the z^* molecules surmounting simultaneously the individual potential energy barriers, $\Delta\mu$, hindering their cooperative rearrangement, which is a temperature-independent constant. This assumption enabled AG to write the single relaxation time, $\tau(T)$, as

$$\tau(T) = \tau_\infty \exp(z^* \Delta\mu/kT) \quad (1)$$

where τ_∞ is the relaxation time at infinite temperature. AG have a linear exponential relaxation function

$$\phi(t) = \exp(-t/\tau(T)) \quad (2)$$

AG further assumed that the configurational entropy associated with the cooperative rearrangement of the z^* molecules, s_c^* , is temperature independent. With the second assumption, AG expressed z^* in terms of the molar configurational entropy S_c

of the macroscopic sample as

$$z^* = N_A s_c^*/S_c \quad (3)$$

where N_A is Avogadro's number. Inserting this equation into the expression for the average relaxation time, eq 1, yields the important result of the AG theory,

$$\tau(T) = \tau_\infty \exp(\Delta\mu s_c^*/kTS_c) = \tau_\infty \exp(C/TS_c) \quad (4)$$

Entropy and thermodynamics being fundamental, the theory of Gibbs and co-workers has a significant impact on the development of research in glass transition in the last 4 decades. The temperature dependence of the configurational entropy, $S_c(T)$, can be calculated from the difference between the heat capacities of the liquid and crystalline states, which can be obtained accurately as a function of temperature by calorimetry.^{5–14} Thus, eq 4 provides a test of the applicability of the AG theory from heat capacity and relaxation data. The predictions of the theory, eq 4, are to some extent in accord with experimental findings, although there are problems that will be discussed later in the next section.

There are new developments in the study of glass transition that seem to indicate that the Adam and Gibbs theory is either inadequate to explain or even at variance with experimental data. Thus, in view of the important role of the AG theory in glass transition research, it is essential to address these problems, which is the primary concern of the present work. The structure of the paper is as follows. First, we point out some of the experimental facts that the AG theory cannot explain. Second, we identify a possible origin of these problems in the AG theory. Finally, we modify the AG theory and show that the predictions of the modified AG model are fully consistent with the experimental facts.

2. Notable Problems of the AG Theory with Experimental Data

Despite the virtue of the AG theory, it has its shortcomings. For example, in the AG theory, all the cooperative rearrange-

ments are identical and they all occur with the same relaxation time. Hence, the relaxation function of the AG theory is a linear exponential of time. On the other hand, the relaxation in most glass-forming liquids near T_g departs from a linear exponential and is well approximated by the Kohlrausch–Williams–Watts (KWW) function,^{15,16}

$$\phi(t) = \exp[-(t/\tau_{\text{exp}})^\beta] \quad (5)$$

where $\beta \leq 1$ and can be temperature dependent. In general, the exponent β is smaller for liquids that have a more rapid T_g -scaled temperature dependence near T_g , although there are exceptions such as propylene carbonate.¹⁷ Moreover, within a family of glass-formers systematic dependence of β on variation of chemical structure has been established.¹⁸ Recent experiments have found that the relaxation of the molecules is dynamically heterogeneous;^{19–22} i.e., there are fast and slow relaxing molecules and they reverse their role within a time approximately equal to $2\tau_{\text{exp}}$.

Obviously, the AG theory in its original form cannot account for any of these properties mentioned in the previous paragraph. Some other shortcomings of the AG theory to be discussed immediately below are of more important concern because they show that the AG theory is at odds with experimental data.

a. Glass-Formers in Confined Space. The study of the molecular dynamics of glass-forming substances in confined space is of fundamental importance. The finite-size effect can be used to test theories of glass transition. The investigation of the effect of finite size on the dynamics of two glass-forming liquids, *ortho*-terphenyl (OTP) and benzyl alcohol, imposed by a matrix with nanometer scale pores was first carried out by Jackson and McKenna using differential scanning calorimetry (DSC).^{23,24} They examined the dependence on the system size of the glass transition temperature, T_g , and the change in the heat capacity, ΔC_p , at T_g . They found that T_g decreases as the pore size decreases, but ΔC_p is independent of pore size. Later, more work showed that the decrease of T_g and the nearly constancy of ΔC_p are independent of the degree of pore filling for both OTP and benzyl alcohol, indicating that a reduction in bulk density or a negative pressure effect is not the cause of the observed results. In fact, from their calculations any reduction in bulk density or negative pressure effect is not large enough to cause the observed changes in T_g .

After the discovery of the finite-size effect on glass transition by calorimetry, other workers^{25–34} have used other experimental techniques to give further insight into the modification of the molecular dynamics. The most commonly used technique is dielectric relaxation, but recently solvation dynamics³³ and photon correlation spectroscopy³⁴ have also been employed to study small-molecule glass-forming liquids confined in glass pores. The benefit these noncalorimetric techniques bring is more direct information on the dispersion of the relaxation over a wider frequency range than calorimetry has offered. For example, dielectric measurement can probe the α -relaxation of the glass-former in the bulk as well as in the confined geometry routinely from 10^{-2} to 10^9 Hz. Photon correlation spectroscopy can do the same in the time domain from a microsecond up to 100 seconds.³⁴ Chemical bonding at the surface can be a problem, particularly for polar liquids. The problem can be avoided by making experimental investigation of liquids confined in porous glass, with inner surfaces that have been chemically treated to replace the $-\text{OH}$ groups on the glass surface with trimethylsilyl groups. Measurements carried out by various workers have found the confined liquid relaxes faster than the bulk liquid. The decrease of the relaxation time becomes

greater on decreasing the confining pore size. The decrease can be very dramatic in fragile liquids such as *ortho*-terphenyl (OTP).³⁴ A reduction of the relaxation time by 6 orders of magnitude from the bulk relaxation time has been found for OTP confined in 2.5 nm pores near the glass transition temperature of bulk OTP.³⁴ These dielectric and photon correlation spectroscopy data are consistent with the decrease in T_g of the confined liquids. More information can be found in refs 34–36.

The observed decrease in T_g of the confined liquids without a reduction in bulk density or a negative pressure effect immediately poses difficulty for the two classical approaches to glass transition, namely the configuration entropy model^{3,4} and the various free volume models. For example, on the basis of the configurational entropy theory of AG, the decrease in entropy due to confinement leads one to expect an increase in T_g . At best, if confinement does not cause a significant decrease in entropy because there is still ample quantity of liquid in the pores, the AG theory predicts no change of T_g , which still cannot explain the experimental data. This important implication of the experimental data that there is a serious difficulty confronting the AG theory was first pointed out by Jackson and McKenna.²⁴ So far, a resolution of this problem encountered by the AG theory has not been given.³⁷ Argument has been offered that the cause of this effect is the reduced size of the confined glass-former, which limits the growth of the temperature-dependent cooperative length scale, which is z^* in the AG theory. However, this argument does not work when applied to the AG theory. This is because the configurational entropy is the fundamental and measurable thermodynamic quantity in the AG theory (eq 4) and it is inconceivable that S_c of the confined liquid can increase, which would follow as a consequence of the argument of a limited growth in z^* according to eq 3.

There is further support of the large reduction of T_g of confined glass-formers from the study of ultrathin free-standing polymer films.^{38,39} For example, in a thin free-standing polystyrene (PS) film with molecular weight $M_w = 767\,000$ and thickness $h = 23.4$ nm. The glass temperature of the thin film was observed to decrease from the bulk T_g of 370 K to 289 K. The end-to-end distance of the polymer chains, $\langle r \rangle$, is 57 nm. The condition $h < \langle r \rangle$ is well satisfied, and therefore the polymer chains are confined in the film. The faster molecular dynamics of the confined polymer have been verified recently by photon correlation spectroscopy and quartz crystal microbalance technique measurements of local segmental motion.³⁹ Since the AG theory was originally proposed for polymers, the reduction of T_g of the confined polymer chains again poses a problem for the AG theory and an explanation has been offered.⁴⁰

b. Thermal-Rheological Complexity of Polymers. In their original paper, AG has shown that their theory can account for the temperature dependence of local segmental motion of polymers by showing that its shift factor, a_T , has the Williams–Landel–Ferry⁴¹ (WLF) form. Although the AG theory does not explicitly address the entire viscoelastic spectrum, its acceptance and conventional wisdom⁴² would lead us to expect that all modes in the spectrum shift with temperature in the same manner as a_T , i.e., thermorheological simple behavior. However, experimentally most amorphous polymers behave otherwise.^{43–46} Irrespective of the molecular weight of the polymer, the shift factor of the local segmental motion, a_T , was found to have a much stronger temperature sensitivity than the rest of the modes in the viscoelastic spectrum. The various thermorheological complex behaviors of polymers were discovered by Plazek and co-workers and amply supported by works of other researchers.⁴⁴

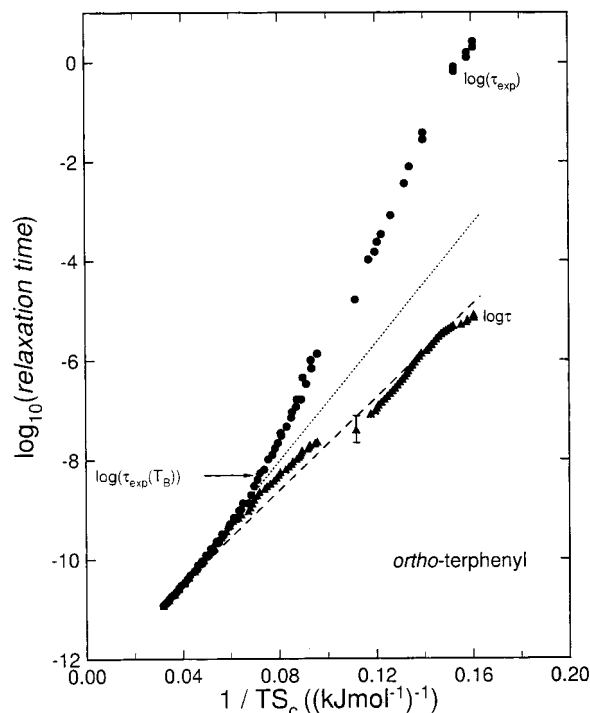


Figure 1. Test of the Adam–Gibbs equation for the α -relaxation time of *ortho*-terphenyl (OTP) at temperatures above T_g . The τ_{exp} data (filled circles) are from dielectric measurements. The horizontal arrow indicates the value of $\log(\tau_{\text{exp}}(T_B))$. The filled triangles are values of $\log \tau$ calculated from τ_{exp} data according to eq 14 of the modified AG model with $\beta(T)$ obtained also from dielectric relaxation data.

Comprehensive reviews of these thermorheological complex behaviors are available.^{44–46} This general behavior cannot be easily explained.⁴³ In the present context of examining the applicability of the AG theory, it is fair to say that this theory made primarily for local segmental motion of polymers cannot *by itself* continue to explain this general viscoelastic property of polymers. Thus, it is desirable to seek some modification of the AG theory, which leads automatically to an explanation of the outstanding viscoelastic anomalies.

c. Deviation from the Proportionality, $\log \tau \propto (TS_c)^{-1}$. Stringent tests of eq 4 of the AG theory have been carried out at temperatures above T_g , where the value of $S_c(T)$ is an equilibrium quantity. Equation 4 predicts a linear relation between $\log \tau$ and $(TS_c)^{-1}$. The first such test was carried out by Magill⁵ for the case of 1,3,5-tri- α -naphthyl benzene in a plot of $\log \eta$ against $(TS_c)^{-1}$. The viscosity η data were obtained from a combination of torsional creep and capillary flow measurements⁴⁷ covering an enormous range of $10^{-2} < \eta < 10^{14}$ poise and $S_c(T)$ was acquired from differential scanning calorimetry. The $\log \eta$ is seen to be linear in $(TS_c)^{-1}$, at low temperatures, but as noted by Magill, the experimental data deviate from the linear relation at the higher temperatures (see Figure 6 of ref 5). Actually, the viscosity contains contributions from both the relaxation time and the shear modulus G_∞ or from the retardation time and the steady-state recoverable compliance J_e . For a single relaxation or retardation time, these quantities are related by $\tau_{\text{exp}}(T) = \eta(T)/G_\infty$ and $\tau_{\text{exp}}(T) = \eta(T)J_e$, respectively. Since experimentally it is found that J_e increases (G_∞ decreases) with temperature, it is not difficult to see that the deviation from linearity found in Magill's plot of $\log \eta$ against $(TS_c)^{-1}$ will be exacerbated in a plot of $\log(\text{retardation})$ or $\log(\text{relaxation time})$ against $(TS_c)^{-1}$. The deviation substantiates the conclusion of an earlier paper by Plazek and Magill⁴⁷ that above T_g the equations resulting from the AG and the free

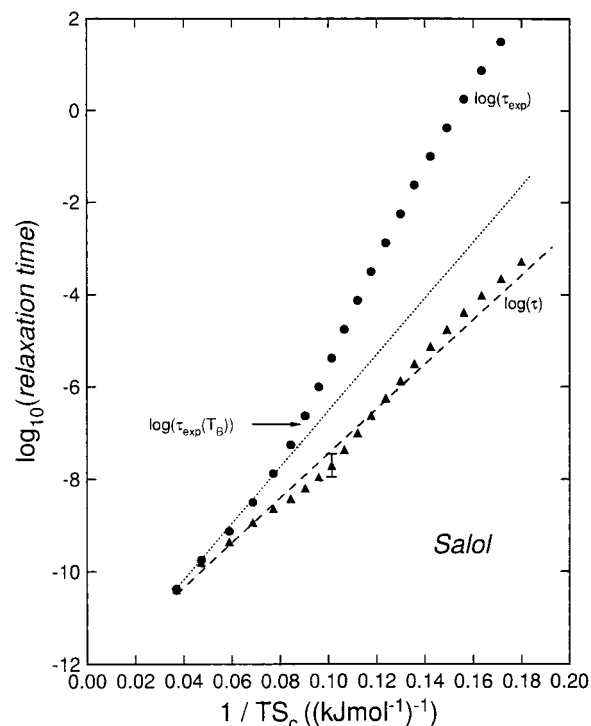


Figure 2. Test of the Adam–Gibbs equation for the α -relaxation time of salol at temperatures above T_g . The rest is the same as in the caption of Figure 1.

volume theories fit the viscosity data over about the same temperature range. Both theories fail to fit the viscosity data at higher temperatures where the deviation from a linear relation between $\log \eta$ and $(TS_c)^{-1}$ appears.

Recent tests of eq 4 were made by Takahara et al.,¹¹ Richert and Angell,⁴⁸ and Yamamuro et al.⁴⁹ in many small-molecule glass-formers using values of $S_c(T)$ obtained from adiabatic calorimetry^{6–12} and $\tau_{\text{exp}}(T)$ from fits of Fourier transform of the derivative of the KWW function (eq 5) to wide-band dielectric relaxation data taken in the typical frequency range 10^{-2} to 2×10^{10} Hz.^{50–56} For fragile liquids that have smaller KWW exponent β like tri- α -naphthyl benzene studied by Magill, the deviation from the linear relation between $\log \tau_{\text{exp}}$ and $(TS_c)^{-1}$ at higher temperatures is reproduced in these recent works.^{48,49} These are shown for several such glass-formers including OTP, salol, triphenyl phosphite (TPP), and an intermediate liquid, 2-methyltetrahydrofuran (MTHF), in Figures 1–4. The dielectric data of OTP, salol, and MTHF are from refs 50–55 and of TPP are from refs 13 and 57. The configurational entropy data for OTP are from ref 7, salol from ref 10, TPP from ref 13, and MTHF from ref 58. The dotted straight line is an extrapolation to lower temperatures of the linear relation between $\log \tau_{\text{exp}}$ and $(TS_c)^{-1}$ established at higher temperatures. The large departure of $\log \tau_{\text{exp}}$ from the dotted line at lower temperatures is clearly evident.

Stickel, Fischer, Richert, and co-workers^{50–52} found the temperature dependence of the α -relaxation time, $\tau_{\text{exp}}(T)$, of many small-molecule glass-forming liquids undergoes a change at a characteristic temperature, T_B . On lowering the temperature, $\tau_{\text{exp}}(T)$ changes from one Vogel–Fulcher–Tammann (VFT) dependence, VFT_{hi} , that holds for $T > T_B$ to another VFT dependence, VFT_{lo} , for $T < T_B$. In glass-formers, which exhibit a β -relaxation of the Johari–Goldstein^{59,60} type, extrapolation of the Arrhenius temperature dependence of its relaxation time, $\tau_\beta(T)$ indicates that it tends to merge into the α -relaxation at a temperature, T_β . Stickel et al. found also that T_B coincides with

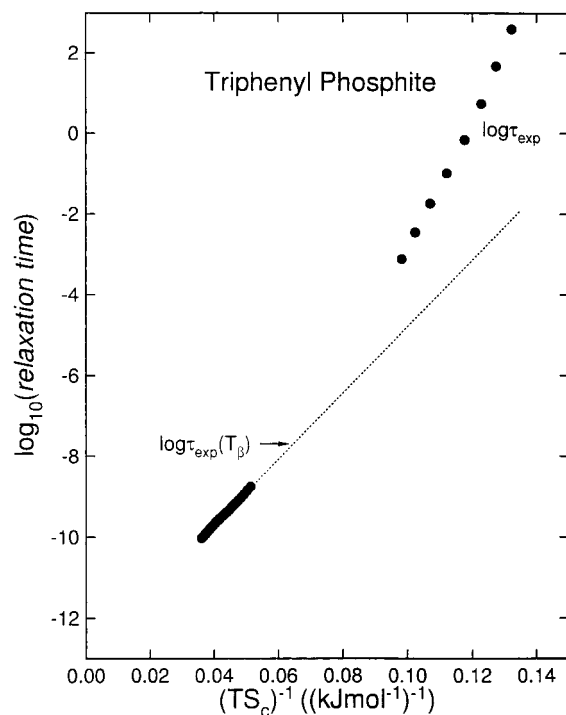


Figure 3. Test of the Adam–Gibbs equation for the α -relaxation time of triphenyl phosphite (TPP) at temperatures above T_g . The τ_{exp} data (filled circles) are from dielectric measurements. The horizontal arrow indicates the value of $\log(\tau_{\text{exp}}(T_\beta))$.

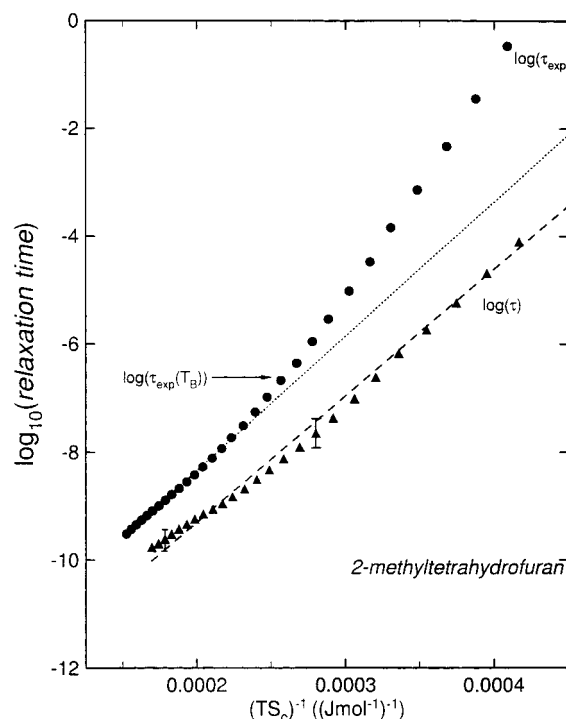


Figure 4. Test of the Adam–Gibbs equation for the α -relaxation time of 2-methyltetrahydrofuran (MTHF) at temperatures above T_g . The rest is the same as in the caption of Figure 1.

T_β . As pointed out by Richert and Angell⁴⁸ and by Yamamuro et al.,⁴⁹ the deviation from the linear relation between $\log \tau_{\text{exp}}$ and $(TS_c)^{-1}$ at higher temperatures starts in the vicinity of T_B or T_β . Although this deviation is general and cannot be ignored, it is remarkable that an approximate linear relation exists between $\log \tau_{\text{exp}}$ and $(TS_c)^{-1}$ over an extensive relaxation time

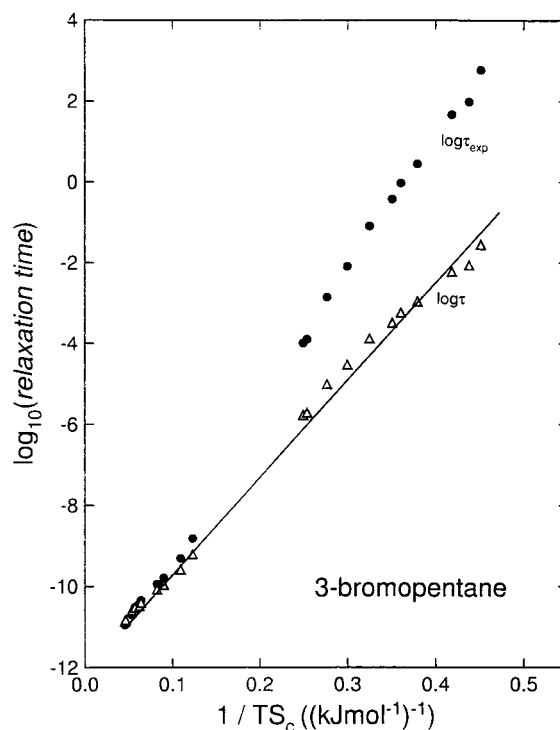


Figure 5. Test of the Adam–Gibbs equation for the α -relaxation time of 3-bromopentane at temperatures above T_g . The rest is the same as in the caption of Figure 1.

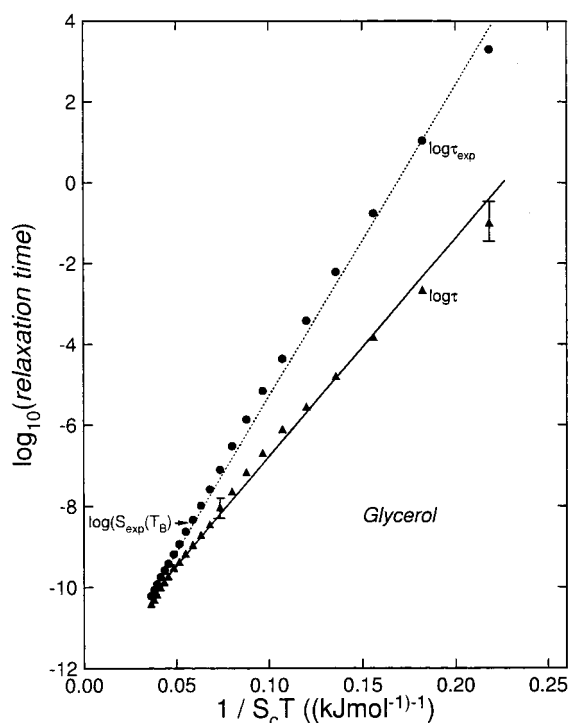


Figure 6. Test of the Adam–Gibbs equation for the α -relaxation time of glycerol at temperatures above T_g . The rest is the same as in the caption of Figure 1.

range, as predicted by the AG theory. This range is given by $1 > \log(\tau_{\text{exp}}/\text{s}) > -8$ for OTP and by $2 > \log(\tau_{\text{exp}}/\text{s}) > -7$ for salol.

Also shown are plots of $\log \tau_{\text{exp}}$ versus $(TS_c)^{-1}$ for glass-formers that have larger KWW β and are less fragile like 3-bromopentane (Figure 5) and glycerol (Figure 6). For 3-bromopentane and glycerol, the dielectric data are from refs 56

and 50 and the configurational entropy from refs 11 and 6, respectively. Contrary to the other glass-formers that have smaller KWW β , the deviation from a linear relation between $\log \tau_{\text{exp}}$ and $(TS_c)^{-1}$ in these two liquids is diminished significantly.

Thus, the AG relation, $\log \tau \propto (TS_c)^{-1}$, is consistent with dielectric and configurational entropy data only over the temperature range $T_g < T < T_B$ or T_β . In general, the AG relation breaks down for $T > T_B$. The extent of the breakdown is larger for liquids that have a smaller value of the KWW exponent β at T_g . Richert and Angell pointed out that the extent of deviations above T_B is correlated with the value of the ratio $\kappa = B_{\text{lo}}/B_{\text{hi}}$, where B_{lo} and B_{hi} are respectively the parameters in VFT_{hi} that holds for $T > T_B$ and VFT_{lo} for $T < T_B$. The last two statements are equivalent because liquids having smaller $\beta(T_g)$ in general have larger κ , as shown in a recent work.⁶¹ Although over the temperature range $T_g < T < T_B$ the dielectric relaxation times cover a large range of approximately 8 decades, $10^{-8} \text{ s} < \tau_{\text{exp}} < 10^0 \text{ s}$, the gravity of the breakdown of the AG relation must not be overlooked. The temperature range $T > T_B$ is important because, according to the AG theory, at high enough temperatures, S_c should approach a constant value $s_c^* N_A$. This constant value was estimated from the S_c vs T curve.^{11,12,49} Substituting the value into eq 2 enables one to calculate $z^*(T)$, the number of molecules in a cooperative rearranging region. Therefore, it is important to address the problem of the breakdown of the AG relation at $T > T_B$ and also to understand why the extent of the breakdown is larger for smaller $\beta(T_g)$.

3. How Realistic Is the AG Theory in Modeling Cooperative Molecular Dynamics?

In reading the paper by AG, one should distinguish the way they build their model, which is more or less arbitrary or at least not unique from the compelling relation between the entropy crisis of Kauzmann and glass transition pointed out by Gibbs in an early paper.¹ The latter was reemphasized by AG in the statement: “The inescapable conclusion of these observations was the one mentioned above, namely that the sluggish relaxation behavior governing T_g is itself a manifestation of the smallness of the entropy (dearth of configurations) in the region immediately above T_2 .” The experimental fact of thermodynamics that the liquid loses its excess configurational entropy on cooling dictates that the motions of the molecules have to be increasingly cooperative involving more and more molecules. But exactly how to model the cooperative motion is not known. AG choose to model the cooperative motion as z^* molecules simultaneously and independently surmounting the individual potential energy barriers, $\Delta\mu$, hindering their rearrangement, resulting in a single relaxation time which has the form given by eq 1. This simultaneous independent motions of a large number z^* of neighboring molecules is unlikely to be carried out to completion because there are interactions between the molecules which inhibit independent movements. On experimental grounds, the recently proven dynamically heterogeneous nature of the molecular motions should cast serious doubt on the feasibility of such a cooperative motion proposed in the AG theory. Hence, there is room for improvement on the formulation of the AG theory. This task will be carried out in the following section.

4. Modified AG Model

The simultaneous and independent motions of z^* neighboring molecules proposed by AG turns out to be the exact analogue of the primitive relaxation of the coupling model (CM).^{62–67}

This analogy was recognized in an earlier attempt⁶⁸ to modify the Adam–Gibbs model for other reasons. This earlier attempt was made in a more restricted context, which is unnecessary. The present description of the modification is more general and preferred. In the coupling model (CM), there exists a temperature-insensitive crossover time t_c with a magnitude determined by the strength of the intermolecular interaction. At times shorter than t_c , all molecular units relax independently of each other and exponentially with time. Following AG, because of the entropy crisis we consider simultaneous and independent motions of z^* molecules. The relaxation function is given by eq 2 and the relaxation time by eq 1. But, according to the CM, this primitive α -relaxation mode cannot continue indefinitely. At and beyond t_c , many-body effects caused by intermolecular interactions slow the relaxation and thus eq 2 holds only for $t < t_c$. This is an important modification, and therefore we rewrite eq 2, adding the explicitly the condition, as

$$\phi(t) = \exp(-t/\tau(T)), \quad t < t_c \quad (6)$$

where $\tau(T)$ given by eq 1 is the primitive α -relaxation time in the CM. We have argued in the previous section that the simultaneous and independent motions of z^* molecules in the AG theory cannot be carried out to completion, as assumed by AG, because of intermolecular interactions. Here, we see how the CM provides a time scale after which this process ceases and a much more complicated and dynamically heterogeneous motion replaces it. After t_c , the intermolecular interactions slow the averaged relaxation process of the z^* molecules and the averaged correlation function assumes the stretched exponential form

$$\phi(t) = \exp[-(t/\tau^*(T))^{1-n}], \quad t > t_c \quad (7)$$

where n , the coupling parameter, lies within the range $0 \leq n < 1$ and its magnitude is a measure of the relaxation slowing down by intermolecular interactions. Equation 7 has exactly the same form as the KWW function of eq 5 used to fit to the experimental data, and naturally τ_{exp} and β therein are identified with τ^* and $(1 - n)$ herein, respectively. To make these relations between experimental quantities and the parameters in the modified AG model perfectly clear, we write explicitly

$$1 - n = \beta \quad (8)$$

and

$$\tau^*(T) = \tau_{\text{exp}}(T) \quad (9)$$

Continuity of $\phi(t)$ at t_c leads to the relation

$$\tau^*(T) = [t_c^{-n} \tau(T)]^{1/(1-n)} \quad (10)$$

between the experimentally observed KWW relaxation time $\tau^*(T)$ or τ_{exp} and the AG relaxation time $\tau(T)$. The existence of a rather sharp crossover time t_c is the most important part of the physics contained in the CM. This and the other predictions of the CM (eqs 6, 7, and 10) had been demonstrated in simple systems modeled by Hamiltonians with interaction that gives rise to chaos.^{62–65} Experimental evidences for the existence of such a crossover in various kinds of systems that have interactions between the relaxing or diffusing units are summarized in ref 67. For molecular liquids of present interest, various experiments^{69–71} and molecular dynamics simulations^{72–74} have found that $t_c \approx 2 \text{ ps}$.

The modified AG model can be summarily described as follows. The relaxation time $\tau(T)$ given by eq 1 in the original

AG theory is not the experimentally observed dielectric relaxation time τ_{exp} , but instead it is the primitive relaxation time of the modified AG model by the CM. The linear exponential function given by eq 2 in the original AG theory governs the observed relaxation only in the short time regime of $t < t_c \approx 2$ ps. The relaxation function that is to be compared with dielectric experiment in the practical time regime of $t > t_c$ is the KWW function of the modified AG model appearing in eq 7 when the condition $\tau^*(T) \gg t_c$ holds. Its characteristic relaxation time $\tau^*(T)$ is related to the AG relaxation time $\tau(T)$ by eq 10, a quantitative relation which has played pivotal roles in various applications of the CM. Obviously, in the modified AG theory we have restored the nonexponential (KWW) nature of the α -relaxation. Although the CM does not describe in any detail the molecular motion, it and hence the modified AG model is consistent with the dynamic heterogeneous property.^{20,75}

5. Consistency of the Modified AG Model with Experiments

We revisit the three experimental facts that the original AG theory has difficulty with, as discussed in section 2, and show that the problems confronting the AG theory disappear when it is replaced by the modified AG model.

a. Glass-Formers in Confined Space. As discussed in section 2.a, the configurational entropy of liquids can either decrease or remain constant when confined and hence cannot explain the large observed decrease in T_g . In the modified AG model when the confined space is sufficiently small, the group of z^* molecules executing the α -relaxation may find its environment quite different than in the bulk liquid. In small confined spaces, the group finds its neighbors are partly the lubricated surface of the pore (or the air surface for the freely standing polymer film) instead of wholly other similar groups. The intermolecular constraints imposed on molecules of the group that are in the proximity of lubricated or free surfaces are mitigated because of the absence of other molecules. Consequently, these molecules have a reduced intermolecular coupling, and in turn there is a reduction of the coupling parameter, n , of the group entering in eqs 7, 8, and 10. The reduction is larger in smaller pores or thinner films because more molecules are affected this way as the surface-to-volume ratio increases. The relation, eq 10, between the α -relaxation time τ^* and the primitive relaxation time τ can be rewritten as

$$\tau^* = \tau[\tau/t_c]^{n/(1-n)} \quad (11)$$

In eq 11, the primitive relaxation time τ is independent of intermolecular coupling, the ratio τ/t_c is much larger than 1, and the exponent $[n/(1-n)]$ is a monotonic increasing function of n . From these facts it is clear that eq 11 predicts a shorter τ^* will result due to a reduction of n in the confined liquid. In other words, the modified AG model predicts a lowering of T_g of glass-forming liquids by confinement, in agreement with experiment.

One may expect that in sufficiently small pores the value of n may be reduced to nearly zero. If this condition holds, then τ^* will be reduced to τ , which can be readily calculated from the expression $\tau = t_c^n(\tau^*)^{1-n}$ because the parameters on the right-hand side are all known. This calculated largest change of τ^* of OTP at temperatures near T_g of bulk OTP has the same order of magnitude^{35,36} as that observed experimentally in OTP confined in 2.5 nm pores, the smallest size studied so far.³⁴ Of course the reduction of τ^* and the corresponding reduction of T_g depend on the size of n of the bulk liquid. This expected

dependence of the size of the effect of confinement on n of the bulk liquid is indeed consistent with the experiment data.³⁶

b. Thermal-Rheological Complexity of Polymers. We have pointed out the various thermorheological complex behaviors of the viscoelastic spectra of amorphous polymers. The original AG theory of glass transition offers no way to explain these intriguing but general properties of amorphous polymers, which do involve the local segmental (α) relaxation addressed in the AG theory.

In the modified AG model, all quantities are determined, in one way or the other, by the coupling parameter n of the α -relaxation. These include the temperature dependence of the α -relaxation time $\tau^*(T)$ and its shift factor a_T^* , which are stronger than that of the primitive AG relaxation time $\tau(T)$ and its shift factor a_T , because the exponent, $[1/(1-n)]$, in eq 10 or in

$$a_T^* = (a_T)^{1/(1-n)} \quad (12)$$

is always larger than 1. The temperature dependence of $\tau(T)$ or a_T is basic because it is determined from thermodynamics consideration (see eq 4) and should enter into the friction factor of the relaxation times of other viscoelastic modes of a polymer. The coupling model follows from a general physical mechanism⁶²⁻⁶⁷ and it applies to other viscoelastic modes. There are similar expressions such as eqs 7 and 10 with the appropriate coupling parameter n_p of the viscoelastic mode p replacing n . Hence, the final temperature dependence of the shift factor, $a_T^{(p)}$, of the relaxation time of mode, p , is determined by

$$a_T^{(p)} = (a_T)^{1/(1-n_p)} \quad (13)$$

Different viscoelastic modes have different intermolecular coupling parameters. Accordingly, from eqs 11 and 12, the shift factors of different modes have different temperature dependences, i.e., thermorheological complex behavior. It turns out, in most amorphous polymers, n of the α -relaxation is the largest among all other coupling parameters.⁴⁴⁻⁴⁶ Thus, the shift factor of the local segmental motion, a_T , has a much stronger temperature sensitivity than $a_T^{(p)}$ of the rest of the other p modes in the viscoelastic spectrum, as found experimentally.^{43,44} Details of the comparison between theory and experiments can be found in a series of papers.⁷⁶

c. Proportionality, $\log \tau \propto (TS_c)^{-1}$, Preserved. If the modified AG model is valid, then the experimentally observed dielectric relaxation time τ_{exp} should be identified with $\tau^*(T)$ like eq 9. Since $\tau^*(T)$ differs from $\tau(T)$ according to eq 10 whenever n is nonzero, τ_{exp} should not be identified with $\tau(T)$ of the original AG theory (eq 4), which predicts the proportionality relation, $\log \tau \propto (TS_c)^{-1}$. Thus, it is not surprising that the comparisons between dielectric data ($\log \tau_{\text{exp}}$) and configurational entropy data $(TS_c)^{-1}$ show deviation from a linear relation for many glass-formers (see Figures 1–5). According to eqs 8–10 of the modified model, $\tau(T)$ can be recovered from the parameters, $\tau_{\text{exp}}(T)$ and $\beta(T)$, used in the fits to the dielectric experimental data by the KWW function (eq 5). The expression is

$$\tau(T) = t_c^{1-\beta(T)}[\tau_{\text{exp}}(T)]^{\beta(T)} \quad (14)$$

where the temperature dependence of β usually found in fitting dielectric data is explicitly written out. The critical test of the modified AG model is whether $\tau(T)$ calculated from $\tau_{\text{exp}}(T)$ and $\beta(T)$ according to eq 14 with $t_c = 2 \times 10^{-12}$ s will bear out the

linear proportionality relation, $\log \tau \propto (TS_c)^{-1}$ of AG in the entire temperature range.

We carry out such a test for each of the glass-formers in Figures 1–6, except TPP, by calculating $\tau(T)$ according to eq 14. For this calculation, we need $\tau_{\text{exp}}(T)$ and $\beta(T)$ from dielectric relaxation data. The relaxation times $\tau_{\text{exp}}(T)$ have already been plotted in these figures, and $\beta(T)$ of these glass-formers can be obtained by fitting dielectric dispersion obtained by wide-band dielectric spectroscopic measurements. At present, the dielectric data of TPP at short $\tau_{\text{exp}}(T)$ are insufficient, and hence a meaningful test has to be deferred to a later time. In general, $\beta(T)$ increases monotonically with temperature and tends to approach the value of unity at high temperatures where $\tau_{\text{exp}}(T)$ becomes short, typically of the order of nanoseconds. The exact temperature dependence of $\beta(T)$ depends on the glass-former. For one thing, the value of $\beta(T_g)$ at the glass temperature may differ from one glass-former to another. However, some structurally similar liquids that contain benzene or phenyl rings such as TNB, OTP, salol, toluene, and TPP have comparable smaller values of $\beta(T_g)$ and similar temperature dependence. While liquids with simpler structures such as glycerol, propylene glycol, and 3-bromopentane have larger values of $\beta(T_g)$. In a recent paper,⁶¹ it was shown for glass-formers having smaller values of $\beta(T_g)$ that on decreasing temperature there is across $T_B \approx T_\beta$ a rapid steplike change of $\beta(T)$ with temperature. The size of the steplike change of different glass-formers decreases proportionately with an increase in the value of $\beta(T_g)$. The temperature dependence of $\beta(T)$ was interpreted⁶¹ in the CM, and now in the modified AG model, as the onset of a significant increase of intermolecular coupling below $T_B \approx T_\beta$.

The calculated $\tau(T)$'s for each glass-former are shown in Figures 1, 2, and 4–6 in a plot of $\log \tau$ against $(TS_c)^{-1}$. The magnitude of the errors introduced into the calculation, mainly from uncertainties of $\beta(T_g)$, are indicated. Within experimental errors, the calculated $\log \tau$ values bear a linear relation with $(TS_c)^{-1}$ throughout the entire temperature range for all glass-formers. Thus, the modified AG model can reconcile dielectric relaxation data with configurational entropy data, and in the process the linear relation between $(TS_c)^{-1}$ and $\log \tau$ of the original AG theory is preserved.

6. Temperature Variation of z^*

For some of the glass-formers at high enough temperatures, the $S_c(T)$ data tends to a constant value, which should be equal to $s_c^* N_A$ according to AG. Having estimated the value of $s_c^* N_A$, the number of molecules z^* in the group executing the α -relaxation can be calculated as a function of temperature from $S_c(T)$ by using eq 3. Such calculation of the temperature dependence of $z^*(T)$ have been done before.^{11,12,49} Here we show $z^*(T)$ as a function of T_B/T (Figure 7) for two fragile liquids, toluene and OTP, which have smaller $\beta(T_g)$, and compare them with that of 3-bromopentane, which has a larger $\beta(T_g)$. In this scaled temperature plot, it is clear that the rise of z^* with T_B/T is significantly more rapid for toluene and OTP than that for 3-bromopentane. Similarly, there are more rapid decreases of β (or increase of the coupling parameter n) and $\log \tau^*$ as a function of T_B/T for toluene and OTP compared with those for 3-bromopentane, glycerol, and propylene glycol. Examples of these contrasting behaviors of dynamic quantities can be found in a recent publication.⁶¹ This similarity suggests that the difference in $z^*(T_B/T)$ between fragile toluene and OTP on one hand and nonfragile 3-bromopentane on the other hand may be the ultimate cause of the corresponding difference between their dynamic properties including $\tau^*(T_B/T)$ and $\beta(T_B/T)$.

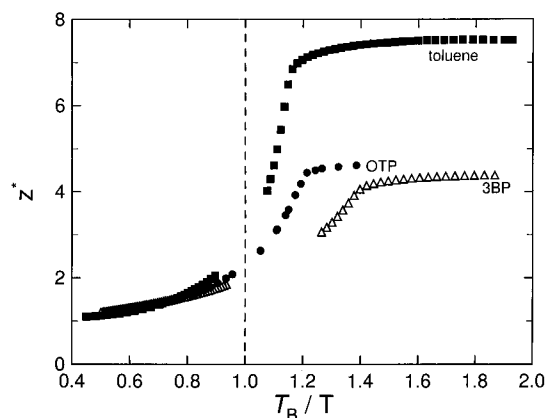


Figure 7. T_B -scaled temperature dependence of z^* , the number of molecules in the group considered together in motion because of the entropy crisis. For toluene T_B is not available, and instead T_β is used.

7. Conclusion

From the discussion in this work, we point out that the Adam–Gibbs (AG) model of glass transition in its original form cannot be reconciled with several important experimental facts. These problems and deficiencies of the AG model are remedied by recognizing that actually its expression for the α -relaxation is most appropriately identified with the primitive relaxation of the coupling model. The many-body molecular dynamics poorly described in the AG theory is improved by combining it with the coupling model. In this manner, the refurbished and modified Adam–Gibbs model is made consistent with all the experimental facts discussed above and constitutes a more complete model of glass transition than the original form. Nevertheless, we should bear in mind that inadvertently the modified AG model has inherited the assumptions (eqs 1–4) in the original AG model, which may or may not be totally correct.

It would be interesting to examine what impact this modified AG model for equilibrium liquid will have when applied to nonlinear enthalpy relaxation within the glass transition temperature range.⁷⁸

Acknowledgment. This work was supported at the Naval Research Laboratory by the Office of Naval Research.

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