

## ARTICLE

## DSC Study on Cooperative Relaxation in 1,2-propanediol

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Cooling rate dependence of the cooperative relaxation in 1,2-propanediol was investigated in terms of the nonlinear Adam-Gibbs (AG) enthalpy relaxation theory using differential scanning calorimetry. The AG parameters were obtained using a curve-fitting method. The results indicated that the model parameters show strong dependence on the cooling rates. Those obtained at higher cooling rates are in good agreement with the published data. The fitting results were used to estimate the microscopic parameters of the cooperative rearranging region (CRR), in particular the size of the CRR ( $z^*$ ) and the configurational state available to it ( $W^*$ ). It was found that the  $W^*$  recommended for polymers led to physically meaningless  $z^*$  for 1,2-propanediol. Johari's method, which was based on the AG theory, yielded around 3 molecules in the CRR, but the  $W^*$  was anomalistically higher than those of polymers. It is difficult to reconcile the Adam-Gibbs'  $z^*$  with the results obtained using Donth's formula. An argument is presented that a new physical meaning should be given to conventional Adam-Gibbs'  $z^*$  for molecular H-bond liquids.

**Key words:** Structure relaxation, Cooperative rearranging region, 1,2-propanediol, Differential scanning calorimetry

## I. INTRODUCTION

Structure relaxation is a nonexponential and nonlinear process. Enthalpy, entropy, volume and other physical properties involved in this process change continuously. In the past two decades, researchers have proposed various phenomenological models to describe the structural relaxation phenomenon [1-3]. In these models, the commonly used expression of the relaxation time is the Narayanaswamy equation [4]. But as noted by Hodge, this expression is empirical and the parameters in this equation have no clear physical interpretation [4,5]. Adam-Gibbs (AG) theory [6] is based on the definition of a cooperative rearranging region (CRR), in which a conformational transition may take place with no interaction with the rest of the material. The time of a conformational rearrangement is calculated in terms of the number of molecules or polymer segments contained in the smallest CRR allowing a conformational rearrangement,  $z^*$ , and the free energy barrier per molecule or chain segment hindering the cooperative rearrangement  $\Delta\mu$ :

$$\tau(T) = A \exp\left(\frac{z^* \Delta\mu}{k_B T}\right) \quad (1)$$

where  $A$  is the pre-exponential factor and  $k_B$  is Boltzmann's constant. The temperature dependence of  $z^*$  is determined by the macroscopic configurational entropy

 $S_c(T)$  [6]:

$$\frac{z^*(T)}{s_c^*} = \frac{N_A}{S_c(T)} \quad (2)$$

where  $s_c^*$  is the entropy of the smallest number of rearranging molecular entities ( $s_c^* = k_B \ln W^*$ ,  $W^*$  is the number of configurational states available to it) and  $N_A$  is Avogadro's number. The nonlinear property of cooperative relaxation was described by introducing the fictive temperature ( $T_f$ ) into the macroscopic configurational entropy expression as [5]:

$$S_c(T_f) = \int_{T_2}^{T_f} \frac{\Delta C_p(T')}{T'} dT' \quad (3)$$

where  $\Delta C_p$  is the configurational heat capacity and  $T_2$  is the temperature at which the configurational entropy vanished. The temperature dependence of  $\Delta C_p$  can be expressed as [5,7]:

$$\Delta C_p(T) = \frac{\Delta C_p(T_2) T_2}{T} \quad (4)$$

where  $\Delta C_p(T_2)$  is the configurational heat capacity at  $T_2$ . According to these equations, the nonlinear AG equation (also called AGV equation [5]) can be deduced:

$$\tau(T, T_f) = A \exp\left[\frac{D}{T(1 - T_2/T_f)}\right] \quad (5)$$

in which

$$D = \frac{N_A s_c^* \Delta\mu}{k_B \Delta C_p(T_2)} \quad (6)$$

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On the other hand, the nonexponentiality implies that there exists a distribution of relaxation time during the relaxation, and this is usually described by the Kohlrausch-Williams-Watts (KWW) equation [4]:

$$\begin{aligned}\phi(t) &= \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right] \\ &= \exp\left\{-\left[\int_0^T \frac{dt'}{\tau(T_f)}\right]^\beta\right\}\end{aligned}\quad (7)$$

where  $\beta(0 \leq \beta \leq 1)$  is the nonexponentiality parameter, inversely related to the width of a distribution of relaxation times. Hodge and Berens gave the following expression of  $T_f$  [8]:

$$T_f(T) = T_0 + \int_{T_0}^T dT' \left\{ 1 - \exp\left[-\int_{T'}^T \left(\frac{dT''}{q\tau(T, T_f)}\right)^\beta\right] \right\} \quad (8)$$

where  $T_0$  is an initial temperature far above  $T_g$  at which the sample is at equilibrium.  $T'$  and  $T''$  are dummy temperature variables, and  $q$  is the heating or cooling rate of DSC. Eq.(5) together with Eq.(8) can be used to computer simulate the thermal histories corresponding to the DSC experiments, producing model curves for the DSC thermograms that usually are expressed in terms of the temperature dependence of normalized specific heat capacity ( $C_p^N = dT_f/dT$ ). These curves can be compared with the experimental ones, and by means of a least squares search routine the set of four parameters included in the models can be determined. Compared to TNM model, the AGV model is physically meaningful and allows one to explore the microscopic parameters in the glass-forming liquids, in particular the  $z^*$ ,  $W^*$ , and  $\Delta\mu$ . This model has been applied to some polymeric glasses with some success since physically reasonable values of the parameters can be obtained [7]. But no systematic discussion is available now on the microscopic parameters in molecular hydrogen-bond (H-bond) liquids. This lack may be because the validity of the AG theory is still in discussion for different materials and only simple and typical molecular liquid has been studied [9].

In the authors' previous work, glass transition and structure relaxation behaviors of ethylene glycol and glycerol and their aqueous solutions were studied using DSC method [10-17]. Here another linear polyalcohol, 1,2-propanediol (called PD hereafter), was chosen for similar study. Though the relaxation kinetics of PD have been studied by different authors [18-21], the cooperative relaxation property is not available now. In the present research, the nonlinear AG theory described above was employed to analyze the cooperative relaxation behavior of PD based on the experimental DSC data. As noted by the authors [22], the nonlinear AG model parameters are not constant for different thermal histories, so it is useful to examine if the model param-

eters are sensitive to the cooling rate. The model parameters obtained using DSC technology can be used to observe the microscopic parameters in PD, in particular the  $z^*$  and  $W^*$ . These results can be compared with the length of cooperativity calculated from the temperature fluctuation theory proposed by Donth [23].

## II. MATERIAL AND METHODS

### A. Reagents and instrumentation

The analytical grade PD (purity >99% by mass) was purchased from Sigma Inc. and used without further purification. Calorimetric measurements were made with a Perkin-Elmer Pyris-Diamond DSC, equipped with nitrogen cooling system (CryoFill™) and Pyris software 5.0 (both Perkin-Elmer). An empty pan was used as reference. The furnace block of DSC was flushed with dry nitrogen gas to avoid condensation of moisture from the air. Helium gas (purity >99.999%) was used as a sample purge at a rate of about 0.02 L/min. The temperature scale of the instrument was calibrated by the melting point of pure ice (273.15 K, onset) and crystallization point of cyclopentane (138.09 K, onset). Also, the enthalpy scale was based on the heat of fusion of pure ice (333.88 J/g). All calibrations were performed by using a scanning rate of 5 K/min.

### B. Temperature programs

All the experiments started at 230 K with the samples in equilibrium. The sample was then cooled down to 115 K, held at these temperatures for just one minute to allow the heat flow return to zero and reheated to 230 K. Six cooling rates ( $q_c=1, 2, 5, 10, 20,$  and  $40$  K/min) and one heating rate ( $q_h=10$  K/min) was used to obtain the heat capacities. The heat flow data were recorded during the heating processes. Cooling rate higher than 40 K/min were not used in this study, since we can not ensure the linearity of the cooling in such a low temperature range.

### C. Calculation and optimizations for the AGV models

A nesting search program written in MATLAB® (with Optimization Toolbox) was used to get the model parameters, with the consideration of the correlation between them. The variable D was arranged in an outside loop, i.e. its value was fixed during each inside search process in which the optimal values of  $A$ ,  $T_2$ , and  $\beta$  were obtained.

At temperatures well below and well above the glass transition, the heat capacity data was assumed to be approximated by a linear function of temperature, i.e. heat capacity in the glass state:  $C_{p,g}(T)=a+bT$  and

heat capacity in the liquid state:  $C_{p,l}(T)=A+BT$ , where  $a$ ,  $b$ ,  $A$ , and  $B$  are constants obtained from the linear least squares fitting to the linear regions of glass and liquid heat capacities. The value of  $T_f$  can be evaluated using Eq.(9) [3]:

$$H(T_2) - H(T) = \int_T^{T_f} C_{p,g}(T')dT' + \int_{T_f}^{T_2} C_{p,l}(T')dT' \quad (9)$$

The terms  $C_{p,g}(T)$  and  $C_{p,l}(T)$  were replaced by  $a+bT$  and  $A+BT$ , respectively. Then, Eq.(9) was integrated and rearranged into the form of a quadratic equation:

$$MT_f + NT_f + Q = 0 \quad (10)$$

Therefore,  $T_f$  can be obtained from solving the quadratic equation with  $M=0.5(b-B)$ ,  $N=a-A$ ,

$$Q = AT_2 + 0.5BT_2^2 - aT - 0.5bT_2 - H(T_2) + H(T) \quad (11)$$

where  $T_2$  is the reference temperature, i.e. the temperature far above  $T_g$  at which the sample is in equilibrium, and  $T$  is the temperature of interest. The difference in enthalpy at  $T_2$  and  $T$ ,  $H(T_2) - H(T)$ , was obtained by numerical integration of the experimental heat capacity data.

### III. RESULTS AND DISCUSSION

#### A. The glass transition

From the heating DSC scans it is possible to calculate the intersection point of the specific enthalpy lines corresponding to the equilibrium and the glassy states, i.e., the limiting fictive temperature ( $T_f'$ ) of the glass as a function of the cooling rate. At higher cooling rates, this temperature is very close to the temperature for which the equilibrium relaxation time is 100 s, as shown in Table I. The value of  $T_f'$  measured after cooling at 40 K/min (166.83 K) is called the glass transition temperature of PD,  $T_g$ . The heat capacity increment during the glass transition can also be obtained from the heating DSC scan. As shown in Table I, these values seem to be constant for different cooling rates.

#### B. Normalized specific heat capacity and simulation

The  $C_p^N(T)$  curves measured after the formation of the glass by cooling from equilibrium at different cooling rates are shown in Fig.1. The main feature in this plot is the maximum in  $C_p^N(T)$ . Its height decreases as the cooling rate increases but even at the highest cooling rate, 40 K/min, a small peak shows. For each cooling rate, the AGV fit gives good approximation to the experimental data. In Fig.2, the effect of cooling rate on the calculated optimized model parameters ( $-\ln A$ ,  $D$ ,

TABLE I Limiting fictive temperature ( $T_f'$ ) and heat capacity increment at  $T_f'$

$q_c/(K/min)$	$T_f'/K$	$T_\tau/K^a$	$\Delta C_p(T_f')/(J/g K)$
1	163.65	167.92	1.010
2	164.25	167.30	0.997
5	165.25	166.12	1.023
10	165.91	166.44	1.018
20	166.53	165.83	1.001
40	166.83	165.15	1.005

<sup>a</sup> The temperature at which  $\tau=100$  s.  $\tau$  is calculated from the best fit results.

$T_2$ , and  $\beta$ ) is shown. From this figure, it is found that the cooling rate has a significant impact on the calculation of AG parameters. The results obtained at lower cooling rates (1, 2, and 5 K/min) show pronounced difference from those obtained at higher cooling rates (10, 20, and 40 K/min). One can also find in Fig.2 that all the four parameters are nearly unchanged at higher cooling rates. This is understandable, since the shape of the steps on experimental  $C_p^N$  curves measured at higher cooling rates show no significant difference.

#### C. Temperature dependence of the relaxation time

Since the different sets of parameters can reproduce the experimental data, as shown in Fig.1, it is difficult to judge which one is the most reasonable. This is due to the correlation that exists between  $D$ ,  $T_2$  and  $\ln A$ . It is well-known that the temperature dependence of the relaxation time in equilibrium can also be described by the linear Vogel-Tammann-Fulcher (VTF) equation ( $T_f=T$  in Eq.(5)):

$$\tau(T) = A \exp\left(\frac{D}{T - T_2}\right) \quad (12)$$

Using the specific-heat spectroscopy data given by the authors [21], one can determine that  $-\ln A=31.77$ ,  $D=2020$ ,  $T_2=114$ , and  $\beta=0.61$ . These results are in good agreement with the values obtained using the dielectric method [24]. In Fig.1 and Fig.2, one can find that the values obtained at higher cooling rates are closer to the published data listed above. In particular, the values of  $T_2$  obtained at higher cooling rates (114 K) seem to be reasonable according to the 'universal' Williams-Landel-Ferry (WLF) [25] relation  $T_g - T_2=51.6$  K. As shown in Table II, the relaxation time calculated using the AGV fitting results can also be divided into two similar groups, one is those calculated at 1, 2, and 5 K/min and the other is calculated at 10, 20, and 40 K/min. In each group, the relaxation time seems to be indistinguishable.

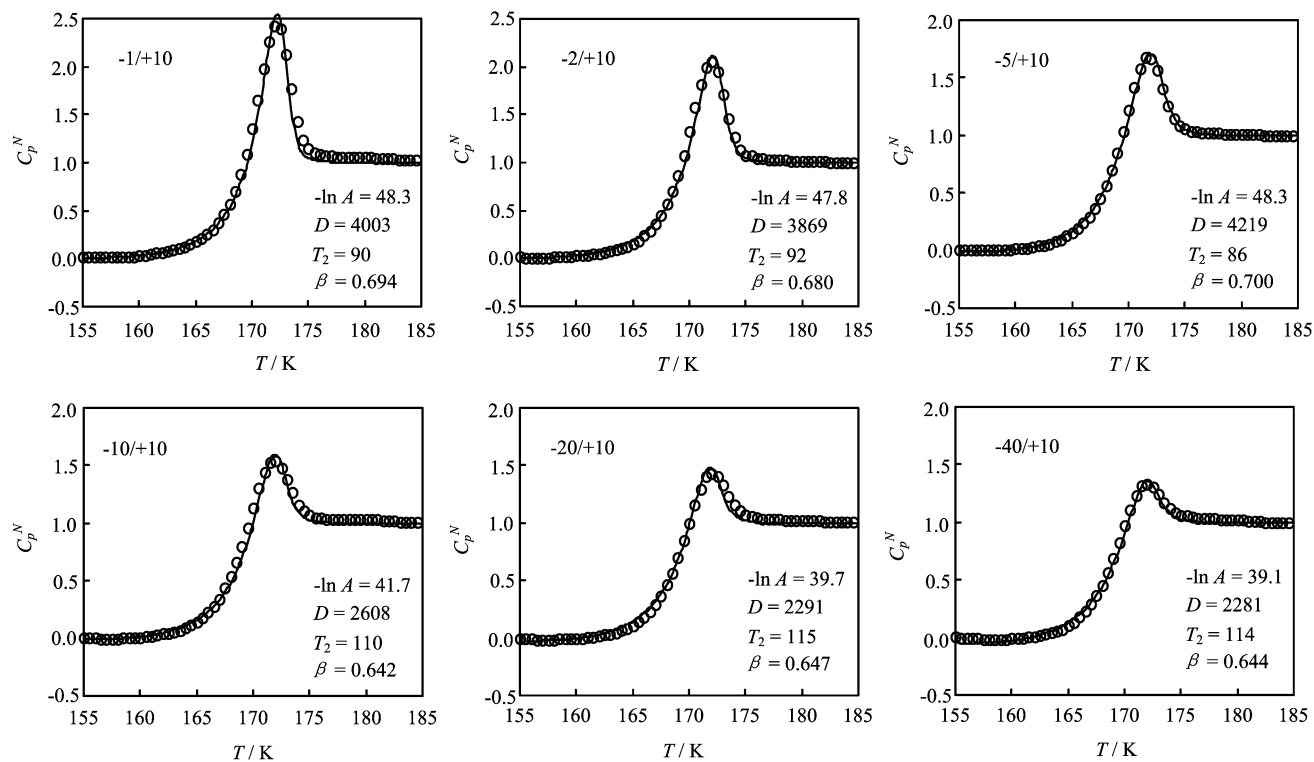


FIG. 1 Experimental data (open circles) and AGV fits (lines) for  $C_p^N$  under indicated cooling and heating rate ( $-q_c/+q_h$ ) for PD. Best fit parameters given in each subfigure.

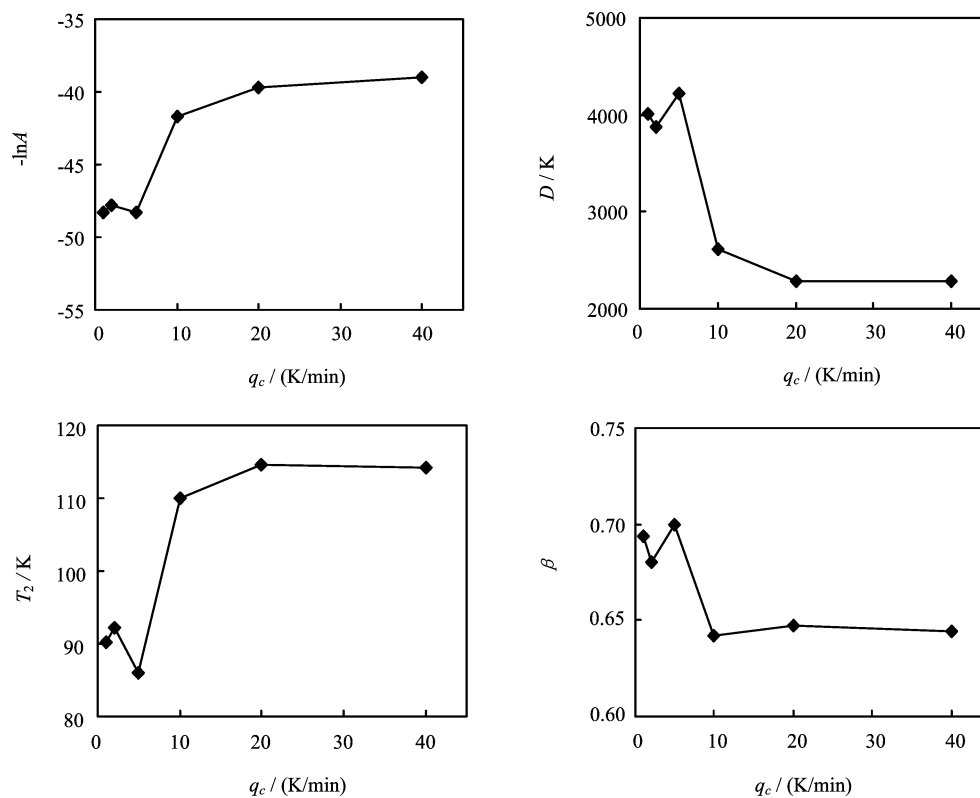


FIG. 2 Best fit AGV parameters as a function of cooling rate for PD.

TABLE II The temperature dependence of the relaxation times ( $\ln\tau$ ,  $\tau$  in s) at different cooling rates

$q_c$ /(K/min)	$\ln\tau$									
	120 K	130 K	140 K	50 K	160 K	170 K	180 K	190 K	200 K	210 K
1	26.38	20.70	15.77	11.50	7.73	3.40	-3.58	-8.06	-11.73	-14.78
2	25.80	20.20	15.34	11.13	7.42	3.11	-3.64	-8.16	-11.85	-14.91
5	25.06	19.48	14.63	10.44	6.79	2.68	-3.33	-7.66	-11.23	-14.22
10	22.82	17.91	13.64	9.97	6.78	2.71	-4.28	-8.98	-12.63	-15.54
20	21.52	16.86	12.83	9.37	6.43	2.52	-4.48	-9.18	-12.77	-15.60
40	20.62	16.08	12.15	8.82	6.07	2.39	-4.28	-8.88	-12.41	-15.20

#### D. Fragility index

The “strong/fragile liquids” classification for liquids was proposed by Angell [26]. The fragility parameter “ $m$ ” can be defined through

$$m = \left. \frac{\partial \lg \tau(T)}{\partial (T_g/T)} \right|_{T=T_g} \quad (13)$$

That is to say, the plot of the logarithm of the relaxation times as a function of  $T_g/T$  can be used to determine the fragility index. According to the fitting results listed in Fig.2, the  $m$  values also show obvious dependence on the cooling rates, but only the value obtained at 40 K/min seems to be close to the published data (see the note of Table III).

TABLE III The  $m$  values calculated using fitting results at different values

$q_c$ /(K/min)	$m^a$	$q_c$ /(K/min)	$m^a$
1	83.5	10	68.7
2	78.1	20	62.1
5	66.8	40	54.9

<sup>a</sup> The  $m$  value of PD given in Ref.[27] is 52.

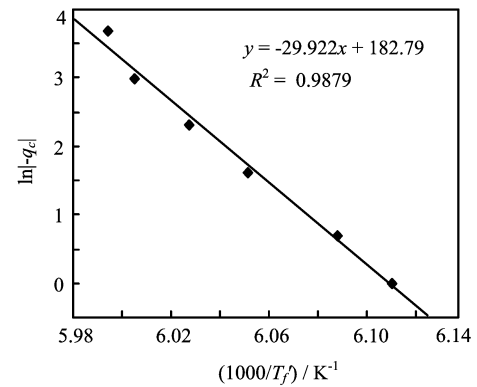
Alternatively,  $m$  can also be calculated from the apparent activation energy around  $T_g$  (usually called  $\Delta h^*$ ):

$$m = \frac{\Delta h^*}{2.303RT_g} \quad (14)$$

The value of  $\Delta h^*$  can be obtained from DSC measurements by observing the cooling rate dependence of  $T'_f$  [28]:

$$\frac{d \ln q_c}{d(1/T'_f)} = -\frac{\Delta h^*}{R} \quad (15)$$

The result shown in Fig.3 yield  $m=77.9$ , which is close to the fitting result obtained at 2 K/min. But it is not clear why  $m$  from the reasonable fitting results (at 40 K/min) are somewhat lower than those obtained via  $\Delta h^*$ .

FIG. 3 The logarithm of cooling rates *vs.* reciprocal of fictive temperature for PD glass.

#### E. The size of CRR from the AGV model

Here we using the model parameters obtained at 40 K/min to investigate the two key quantities of the AG theory, namely the size of the cooperatively rearranging regions ( $z^*$ ) and the temperature-invariant energy term per mole ( $\Delta\mu'$ ). However, some approximations or assumptions must be performed first for the expressions of  $\Delta C_p(T)$  and  $s_c^*$ . Since the results discussed here are not particularly sensitive to the form of  $\Delta C_p(T)$ , Eq.(4) will be used throughout the present discussion. Thus the following expression can be obtained:

$$\Delta\mu' = \frac{D\Delta C_p(T_g)T_gM_s}{T_2 \ln W^*} \quad (16)$$

$$z^*(T_g) = \frac{s_c^*N_A}{S_c(T_g)} = \frac{R \ln W^*}{\Delta C_p(T_g)(T_g/T_2 - 1)M_s} \quad (17)$$

where  $M_s$  is the molecular weight. There must be a minimum of two configurations available for relaxation to occur (those before and after rearrangement), so  $W^*$  is originally been taken to be 2 [6]. Hodge suggested that  $W^*$  might be approximated as  $2^3$  [3,7]. Furthermore,  $W^*=2^4$  also has been used to analyze the enthalpy relaxation in epoxy systems [29]. Although these assumptions implied that different sys-

tems would possess the same  $s_c^*$  value, it led to reasonable  $z^*(T_g)$  values according to their physical meanings [7] and consistent with the expected trend of the structure factors influencing the enthalpy relaxation process [30]. In particular, the direct observation of the cooperative relaxation in polyvinyl acetate (PVAc) using nanometer-scale probing confirmed that molecular clusters switched among 2-4 configurations near the glass transition [30]. But for nonpolymeric molecular liquids, it is not clear which value of  $W^*$  should be chosen. Table IV gives the values of  $\Delta\mu'$  and  $z^*$  calculated for each  $W^*$ . It is evident that all three  $W^*$  values recommended for polymeric glasses are not acceptable for PD, since they yield  $z^*$  less than one. Furthermore, the values of  $\Delta\mu'$  seem to be unreasonable according to its physical meaning [6,7].

TABLE IV The temperature-invariant energy  $\Delta\mu'$  and  $z^*(T_g)$  calculated for each  $W^*$

$W^*$	$z^*$	$\Delta\mu'/(kJ/mol)$
2	0.163	368.41
2 <sup>3</sup>	0.488	122.80
2 <sup>4</sup>	0.650	92.10

Johari argued that in addition to  $\Delta\mu'$ ,  $W^*$  is also a characteristic property of the liquid [31]. According to the relaxation time expression of Eq.(1) and Eq.(9), Johari author gives the following expressions [31]:

$$z^*(T) = \frac{1}{1 - T_2/T} \quad (18)$$

$$\Delta\mu' = RD \quad (19)$$

Though these estimates are approximate, they are consistent with the thermodynamic and kinetics relations. In particular, Eq.(18) is physically reasonable both at the high temperature limit ( $z^* \rightarrow 1$ ) and  $T_2$  ( $z^* \rightarrow \infty$ ). According to this expression,  $z^*$  is determined only by the ratio  $T_2/T$ . This can be used to estimate  $W^*$  according to Eq.(17) and recalculate  $\Delta\mu'$  according to Eq.(16) (which is equivalent to Eq.(19) if Eq.(18) is reasonable). These calculations produce  $z^*(T_g)=3.158$  and  $\Delta\mu'=18.96$  kJ/mol. But this calculation yields  $W^*=705048$  according to Eq.(17), which seems to be anomalistically higher than those of polymers. It is doubtful, as for PD, that so many configurational states are available for only three molecules in the CRR.

#### F. The size of the CRR from the temperature fluctuation theory

Donth proposed a formula for the volume  $V_a$  of the CRR on the basis of his temperature fluctuation theory [23,32,33], which is

$$V_a = \frac{kT_g^2}{\rho\delta T^2} \left( \frac{1}{C_{p,g}} - \frac{1}{C_{p,l}} \right) \quad (20)$$

where  $\rho$  is the density and  $\delta T$  is the mean temperature fluctuation in the CRR. The data available from the DSC results are enough to estimate the number of molecules included in the CRR using Eq.(20):

$$N_{\text{CRR}} = \frac{RT_g^2 \Delta C_p(T_g)}{\bar{C}_p^2 \delta T^2 M_s} \quad (21)$$

where  $\bar{C}_p$  is the average specific heat of liquid and glass at  $T_g$ . The value of  $\delta T$  can be approximated as  $\Delta T/2.5$ , where  $\Delta T$  is defined as the temperature interval according to the  $C_p(T)$  curve measured upon heating DSC scan [33]. This method yields  $N_{\text{CRR}}=355$  (with the accuracy of 85%-125% [34]). For PVAc, it shows that the size of CRR calculated using AG theory is within an order of magnitude of that obtained using Donth's method [35], but in the present study, there seems to be no possibility of reconciling  $N_{\text{CRR}}$  with  $z^*$  in the AG sense. One possible explanation is that the result obtained by Donth's formula is not the size of CRR, but the length scale of the dynamic heterogeneities, which can be seen as the upper limit of the scale length of CRR [36]. Though the 'upper limit' assumption is correct according to the experimental results, we can argue that it cannot give any helpful information to investigate  $z^*$  in PD, since  $N_{\text{CRR}}$  is dramatically larger than  $z^*$ . In fact, to date it is not clear how to relate the length scale for dynamic heterogeneity to the size of CRR.

NMR is another useful method to investigate the length scale of the dynamic heterogeneities, which seems to be more direct than the calorimetry [36]. As noted by Reinsberg *et al.*, NMR experiments carried out on three glass formers including H-bonded liquids near  $T_g$  produced consistent results with the values obtained using Donth's formula [37]. As mentioned in the discussion above,  $z^*$  obtained using Johari's formula is somewhat reasonable according to its physical meaning. The question is how to reconcile the big difference between 3.15 and 355. One possible solution is that  $z^*$  can only be used to describe the CRRs in some polymers other than the molecular H-bond liquids. So it is neither possible nor necessary to reconcile these two parameters to each other in the molecular H-bond liquids.

Alternatively, a new physical meaning could be given to  $z^*$  in molecular H-bond liquids. Dielectric relaxation study of monohydric alcohols and water indicated that hydrogen bonded 'network clusters' play important roles in the relaxation processes [38]. Here, if  $z^*$  is regarded as number of hydrogen bonded clusters in the CRR but not the number of molecules, the question mentioned above will become explicable. That is to say, 3.15 molecular clusters in average are included in one CRR at  $T_g$  and each cluster consists of about 113 PD molecules. Base on this assumption, one can find that the problem raised in  $W^*$  is explicable, because unlike the segments of polymers, the molecular clusters connected with H-bonds have no fixed chemical structure. Their cooperative motions must be accompanied by the

breaking and re-bonding of the H-bond, so the CRRs in H-bond liquids must possess more spatial configurational states than those in polymers.

#### IV. CONCLUSION

The nonlinear Adam-Gibbs model used in this work is able to reproduce the DSC structural relaxation behavior of 1,2-propanediol. The model parameters, relaxation time and fragility index show strong dependence on the cooling rates. In particular, the model parameters and the relaxation times calculated at lower cooling rates show significant difference from those obtained at higher cooling rates. In terms of the curve-fitting results, it can be concluded that conventional AG theory can not produce physically reasonable size of CRR in the present systems. It is difficult to reconcile the results obtained using Johari's method with those obtained by Donth's formula. An argument is made that a new physical meaning should be given to  $z^*$  in molecular H-bonded liquids.

#### V. ACKNOWLEDGMENTS

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