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Composition dependence of the Adam–Gibbs cooperative relaxation parameters in glycerol aqueous solutions

Cai Gao [a,*], Tie-Jun Wang [a], Xiang-Nong Liu [a], Guo-Yan Zhou [b], Tse-Chao Hua [b]

[a] *School of Mechanical and Automotive Engineering, Hefei University of Technology, Hefei 230009, China*
[b] *Institute of Cryomedicine and Food Refrigeration, University of Shanghai for Science and Technology, Shanghai 200093, China*

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Abstract

Cooperative relaxation of glycerol and its four aqueous solutions (60%, 70%, 80% and 90% by mass) has been investigated in terms of the nonlinear Adam–Gibbs (AG) enthalpy relaxation theory using differential scanning calorimetry (DSC). The AG parameters were obtained using curve-fitting method. The results indicated that the relaxation time of glycerol/water mixtures is water-sensitive. With the changing of water content, regular trend was found in both the equilibrium and the glassy state. 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^*). The results showed that the W^* recommended for polymers led to physically meaningless z^* for glycerol and its aqueous solutions. Johari's method, which still based on the AG theory, yielded three to four molecules in the CRR. But the W^* is anomalistically higher than those of polymers. With the changing of the water content, the size of CRR estimated using Donth formula seemed to be reasonable according to the analysis of the apparent activation energy (Δh^*), the distribution parameter the of relaxation times (β). But it is difficult to reconcile the Adam–Gibbs' z^* with the results obtained using Donth's formula.

Keywords: Cooperative relaxation; Cooperative rearranging region (CRR); Glycerol; Aqueous solutions; Differential scanning calorimetry (DSC)

1. Introduction

The structure relaxation is a nonexponential and nonlinear process, during which enthalpy, entropy, volume and other physical properties 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 [4,5], this expression is empirical and the parameters in this equation have no clear physical interpretation. The Adam–Gibbs theory [6] provides an alternative expression for the relaxation time. It 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 $\Delta\mu$:

$$\tau(T) = A \exp\left(\frac{z^*\Delta\mu}{k_\mathrm{B}T}\right) \tag{1}$$

where A is the pre-exponential factor and k_B is the Boltzmann's constant. The temperature dependence of z^* is determined by the macroscopic configurational entropy $S_\mathrm{c}(T)$ [6]:

$$\frac{z^*(T)}{s_\mathrm{c}^*} = \frac{N_\mathrm{A}}{S_\mathrm{c}(T)} \tag{2}$$

where s_c^* is the entropy of the smallest number of rearranging molecular entities ($s_\mathrm{c}^* = k_\mathrm{B}\ln W^*$, W^* the number of configurational states available to it) and N_A is the Avogadro's number. The nonlinear property of cooperative relaxation was described by introducing the fictive temperature (T_f) into the macroscopic

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[*] Corresponding author. Tel.: +86 551 5566584; fax: +86 551 2901750.
E-mail address: gao_cai@hotmail.com (C. Gao).

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configurational entropy expression as [5]:

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

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

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

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

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

in which

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

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]:

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right] \tag{7}$$

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

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

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. 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. The AG equation 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 equation has been applied to some polymeric glasses with some success since physically reasonable values of the parameters can be obtained [7]. But no systematically discussion is available now on the microscopic parameters in molecular hydrogen-bond (H-bond) liquids. It maybe because the validity of the AG expression is still in discussion for different materials and only simple and typical molecular liquid has been studied [9].

Glycerol is a typical H-bond liquid and is often used as model system for glass transition and relaxation kinetics study. Its relaxation behavior has been studied by adiabatic calorimetry [10], NMR [11], specific heat spectroscopy (HCS) data [12,13] and DSC/TMDSC [14,15], but it is difficult to find consistent results in these previous studies. In the present paper, glycerol (called G100 hereafter) and its four aqueous solutions (60%, 70%, 80% and 90% by mass just for convenience, called G60, G70, G80 and G90 respectively), which could be vitrified completely under practical cooling rates, are chosen for DSC analysis. The nonlinear AG equation described above is employed to model the experimental data, though its model parameters are not constant for different thermal history [16]. This work assumes the existence of the CRR in small-molecule H-bond liquids, keep in mind that only the polymer's CRR was confirmed by direct observation [17]. The aim of this work is to explore if the cooperative relaxation behavior of the homologous glycerol aqueous solution series is water-sensitive under the uniform thermal history, in particular the general feature of the concentrations dependence of the CRR size and the number of states available to it. These results are compared with the length of cooperativity calculated from the temperature fluctuation theory proposed by Donth [18].

2. Material and methods

2.1. Reagents

The analytical grade glycerol was purchased from Sigma Inc. and was used without further purification. The aqueous solutions were prepared using double distilled water. Standard aluminum pans (Perkin-Elmer) were used in all DSC experiments and all samples were around 5 mg.

2.2. Equipments

Calorimetric measurements were made with a Perkin-Elmer Pyris-Diamond DSC, equipped with nitrogen cooling system (CryoFill^{TM}) 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 was used as sample purge at a rate of about 20 ml/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). And the enthalpy scale was based on the heat of fusion of pure ice (333.88 J/g). All calibrations were performed by using scanning rate of 5 K/min.

2.3. Temperature programs

All the experiments started at $T_g + 50$ K with the samples in equilibrium. The samples were then cooled down to $T_g - 50$ K, hold at these temperatures for just 1 min to allow the heat flow return to zero and reheated to $T_g + 50$ K. Five cooling rates ($q_c = 1, 2, 5, 10, 20$ K/min) and one heating rate ($q_h = 10$ K/min) were used for each sample. To calculate the heat capacities, the heat flow data of empty pans were also obtained under the same

Table 1
Glass transition temperature (T_g) and heat capacity increment at T_g

Solutions	T_g (K)[a]	$T_{g\tau}$ (K)[b]	$\Delta C_p(T_g)$ (J/g K)
G60	162.1	162.3	1.02
G70	168.3	167.1	0.97
G80	174.0	173.8	0.96
G90	181.5	181.0	0.94
G100	191.4	191.0	0.94

[a] The intersection point of the enthalpy lines corresponding to the liquid and the glass $q_c = q_h = 10$ K/min.

[b] The temperature at which $\tau = 100$ s.

temperature programs. The heat flow data were recorded during the heating processes. Different cooling rates were only used to calculate the apparent activation energy and dynamic fragility. The heat capacities obtained at equal cooling and heating rate, $q_c = q_h = 10$ K/min were used in curve-fitting processes and all the other calculations.

2.4. Curve-fitting and uncertainties

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 outside loop, i.e. its value was fixed during each inside search process in which the optimal values of A, T_2 and β were obtained. In the present study, we found the main uncertainties of the calculations were derived from experimental scatter among the parallel samples and those produced during the curve-fitting procedures. The errors produced by the repeat analysis for the same sample were negligible. For each concentration, five samples were prepared for the same DSC analysis.

3. Results and discussion

The glass transition temperature of each solution has been defined as the temperature of the intersection of the enthalpy lines corresponding to the liquid and the glassy states (the limiting fictive temperature, T_f'). As show in Table 1, this temperature is very close to the temperature for which the equilibrium relaxation time is 100 s. The glass transition temperature of glycerol aqueous solutions decreased with the increase of water content.

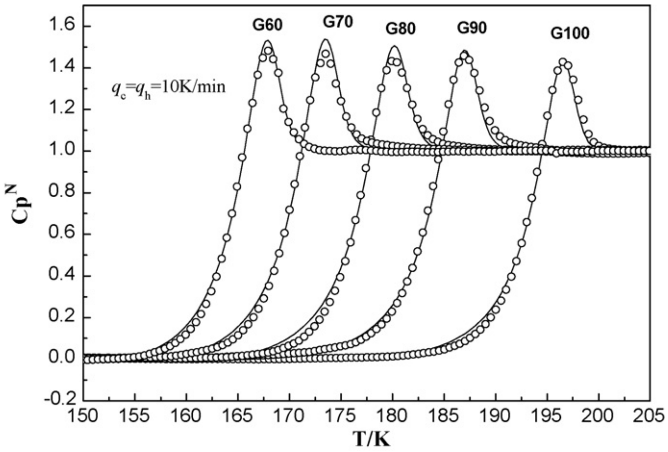

Fig. 1. Experimental normalized heat capacities (open circles) and the prediction (solid lines) of the model with the parameters according to Table 2.

The experimental normalized specific heat capacity curves and the best-fit ones are given in Fig. 1. It can be said that the agreement between the experimental and the model-simulated curve is very good. The AG model parameters obtained by the curve-fitting method are reported in Table 1. The values of $-\ln A$ and D are slightly higher in pure glycerol than those in the aqueous solutions. But both $-\ln A$ and D seem to be unchanged in aqueous solutions. It was found that T_2 decreased with increasing water content while β changed inversely. The difference between our results and those obtained also by DSC at different temperature program [15] (see the notes of Table 2) indicates that the model parameters are sensitive to thermal history. It is well-known that the temperature dependence of the relaxation time in equilibrium can be described by the linear Vogel–Tammann–Fulcher (VTF) equation ($T_f = T$ in Eq. (5)):

$$\tau(T) = A \exp\left(\frac{D}{T - T_2}\right) \tag{9}$$

The VTF parameters for G100 have been given by the authors [13] using HCS data ($-\ln A = 33.62$, $D = 2500$ K, $T_2 = 128 \pm 5$ K and $\beta = 0.65$), but only the values of D seems to be close to our results. In particular, the value β obtained by HCS is 0.65, which seems to be significantly higher than the value obtained by DSC. One possible explanation is that the measurement of HCS is frequency-dependent [3]. The values of T_2 listed in Table 2 seem to be reasonable according to the 'universal' Williams–Landel–Ferry (WLF) [19] relation $T_g - T_2 = 51.6$ K. The value of T_2 of glycerol obtained by us is in good agreement with its Kauzmann temperature, $T_K = 136.7$ K [20].

The temperature dependence of the relaxation time was calculated with the model equations for the heating of the samples at 10 K/min from $T_g - 50$ K to equilibrium, using the parameters

Table 2
The model parameters found for each solution

Solutions	$-\ln A$ (s)	D (K)	T_2 (K)	$T_g - 51.6$ (K)	β
G60	34.91 ± 0.149	2297 ± 183.8	103.23 ± 1.210	110.5	0.640 ± 0.0184
G70	34.96 ± 0.573	2238 ± 89.0	110.51 ± 1.075	116.7	0.627 ± 0.0050
G80	35.52 ± 0.422	2265 ± 172.4	117.33 ± 0.683	122.4	0.606 ± 0.0017
G90	36.11 ± 0.505	2188 ± 69.7	128.96 ± 0.907	129.9	0.577 ± 0.0023
G100[a]	42.80 ± 1.204	2545 ± 190.2	137.33 ± 1.413	139.8	0.554 ± 0.0094

[a] The values of ln A = −34.19 s, $D = 2179$ K, $T_2 = 134$ K and $\beta = 0.51$ are given in literature [15] (20 K/min).

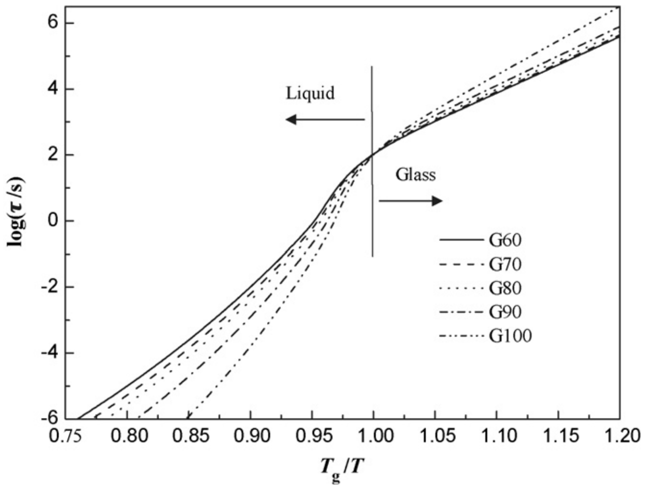

Fig. 2. Temperature dependence of the relaxation times determined with the model parameters according to Table 2.

of Table 2. These results are shown in Fig. 2. It shows that the relaxation processes in the solutions with higher water content are slower in equilibrium but faster in glassy state. The curves of structure relaxation time seem to be a lever pivoted on a fixed point with the changing of water content. The fitting results of the relaxation time can be used to evaluate the Angell's fragility [21]:

$$m = \left.\frac{\mathrm{d}\log\tau}{\mathrm{d}(T_\mathrm{g}/T)}\right|_{T=T_\mathrm{g}} \tag{10}$$

The trend between m and composition can be easily obtained by direct viewing of Fig. 2. It is clear that the solutions with higher concentration are stronger than those with lower concentration. Alternatively, m can also be calculated from the namely apparent activation energy around T_g (usually called Δh^*):

$$m = \frac{\Delta h^*}{2.303RT_\mathrm{g}} \tag{11}$$

The value of Δh^* can be obtained from DSC measurements by observing the cooling rate dependence of T_g [22]:

$$\frac{\mathrm{d}\ln|q_\mathrm{c}|}{\mathrm{d}(1/T_\mathrm{g})} = -\frac{\Delta h^*}{R} \tag{12}$$

In Table 3, one can find that m obtained using Eq. (11) decreased with increasing water content, which is consistent with the trend shown in Fig. 2. Since Δh^* can be related to AG parameters [3,5], so m can also be estimated using the following expression:

$$m = \frac{DT_\mathrm{g}}{2.303(T_\mathrm{g}-T_2)^2} \tag{13}$$

The values of m calculated using Eq. (13) are given in Table 3. Though this method yields somewhat larger results than those obtained via Δh^*, it still gives the same prediction that the increasing of water content can lower the fragility of the solutions. In addition, the correlation between m and β shown in this study is consistent with that found by the authors [23].

The values in Table 2 allow us 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 $\Delta C_p(T)$ and Eq. (4) will be used throughout the present discussion. Thus the following expression can be obtained:

$$\Delta\mu' = \frac{D\Delta C_p(T_\mathrm{g})T_\mathrm{g}M_\mathrm{s}}{T_2\ln W^*} \tag{14}$$

$$z^*(T_\mathrm{g}) = \frac{s_\mathrm{c}^* N_\mathrm{A}}{S_\mathrm{c}(T_\mathrm{g})} = \frac{R\ln W^*}{\Delta C_p(T_\mathrm{g})(T_\mathrm{g}/T_2-1)M_\mathrm{s}} \tag{15}$$

where M_s is the molecular weight for pure compound or equivalent molecular weight for mixture. 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 [3,7] suggested that W^* might be approximated as 2^3. Furthermore, $W^* = 2^4$ also has been used to analyze the enthalpy relaxation in epoxy systems [24]. Although these assumptions imply that different systems will possess the same s_c^* value, it led to reasonable $z^*(T_\mathrm{g})$ values according to their physical meanings [7] and consistent with the expected trend of the structure factors influencing the enthalpy relaxation process [24]. In particular, the direct observation of the cooperative relaxation in polyvinyl acetate (PVAc) using nanometre-scale probing confirms that molecular clusters switched among 2–4 configurations near the glass transition [17]. But for nonpolymeric molecular liquids, it is not clear which the value of W^* should be chosen. Table 4 gives the values of $\Delta\mu'$ and z^* calculated for each W^*. It is evident that all the three W^* values recommended for polymeric glasses are not acceptable for glycerol and its aqueous solutions, since they yield z^* less than one in the CRR. Johari [25] argued that in addition to $\Delta\mu'$, W^* is also

Table 3
The apparent activation energy and fragility

Solutions	$\Delta h^*/R$ (kK)	m[a]	m[b]
G60	13.0	34.8	46.7
G70	14.5	37.4	49.0
G80	16.7	41.6	53.3
G90	19.2	46.0	62.5
G100	23.8	54.0	72.3

[a] Calculated using Eq. (11).
[b] Calculated using Eq. (13).

Table 4
The temperature-invariant energy $\Delta\mu'$ (kJ/mol) and $z^*(T_\mathrm{g})$ calculated for each W^*

Solutions	$W^* = 2$		$W^* = 2^3$		$W^* = 2^4$	
	$\Delta\mu'$	z^*	$\Delta\mu'$	z^*	$\Delta\mu'$	z^*
G60	184.7	0.29	61.6	0.85	46.2	1.14
G70	196.5	0.28	65.5	0.83	49.1	1.10
G80	234.9	0.25	78.3	0.74	58.7	0.98
G90	272.3	0.23	90.8	0.69	68.1	0.92
G100	442.5	0.17	147.5	0.51	110.6	0.68

Table 5
$z^*(T_g)$, W^* and $\Delta\mu'$ (kJ/mol) calculated using Johari' method (see text)

Solutions	$z^*(T_g)$	W^*	$\Delta\mu'$
G60	2.75	814	19.1
G70	2.91	1,509	18.6
G80	3.07	5,684	18.8
G90	3.45	32,031	18.2
G100	3.54	1,977,086	21.2

a characteristic property of the liquid. According to the relaxation time expression of Eqs. (1) and (9), the author gives the following expressions [25]:

$$z^*(T) = \frac{1}{(1 - T_2)/T} \tag{16}$$

$$\Delta\mu' = RD \tag{17}$$

Though these estimates are approximate, they are consistent with the thermodynamic and kinetics relations. In particular, Eq. (16) is physically reasonable both at the high-temperature limit ($z^* \to 1$) and T_2 ($z^* \to \infty$). According to this expression, z^* is determined only by the ratio T_2/T. This can be used to estimate W^* according to Eq. (15) and re-calculate $\Delta\mu'$ according to Eq. (17) (it is equivalent to Eq. (14) if Eq. (16) is true) and the results are listed in Table 5.

These calculations produce the values of $z^*(T_g)$ in the range 2.75–3.54. Since the values of $\Delta\mu'$ only determined by D, so no obvious change is found for different compositions according to the fitting results. This trend is inconsistent with the change in the apparent activation energy Δh^* (Table 3). It maybe because that $\Delta\mu'$ and Δh^* represent activation energies that are averaged in different dimensions, and the former stems from the molecular rearrangement within the CRR, whereas the latter is the average activation energy for all the CRRs. Inconsistent results between $\Delta\mu'$ and Δh^* were also found in epoxy systems [24]. As shown in Table 5, the values of W^* seems to be anomalistically higher than those of polymers. It is doubtful, as for glycerol, that so many configurational states are available for only three or four molecules in the CRR. It is also not clear why W^* decreased dramatically with increasing water content. Furthermore, the physical meaning of z^* is amphibolous since two kinds of molecules exist in the glycerol aqueous solution.

With the questions raised above, we adopt another approach proposed by Donth [14,18] to estimate the volume of the CRR (V_{CRR}):

$$V_{\mathrm{CRR}} = \xi_{\mathrm{CRR}}^3 \approx \frac{k_B T_g^2 \Delta C_p(T_g)}{\bar{C}_p^2 \rho \delta T^2} \tag{18}$$

where ξ_{CRR} is the length scale the CRR, k_B is the Boltzmann constant, $\bar{C}_p$ is the average specific heat of liquid and glass at T_g, ρ is the mass density, and δT is the mean-square temperature fluctuation of CRR. δT can be approximate to $\Delta T/2.5$ [26], where ΔT defines as the temperature interval according to the $C_p(T)$ curve measured upon heating DSC scan, as shown in Fig. 3. This method yields ξ_{CRR} (with the accuracy of 85–125% [14]) values of 2.1, 2.4, 2.6, 2.8 and 3.0 nm for G60, G70, G80, G90 and G100 respectively. This trend seems to be reasonable according to Δh^*. It is believed that the relaxation motion of the smaller CRRs is easier than those larger ones, so lower values of Δh^* were found in the systems with high water content. It is also understandable that in small CRR, molecules might move with a lesser range of mobility than those in large CRR. Thus, a smaller ξ_{CRR} could be associated with a smaller β. This is in good agreement with the fitting results of β (Table 2).

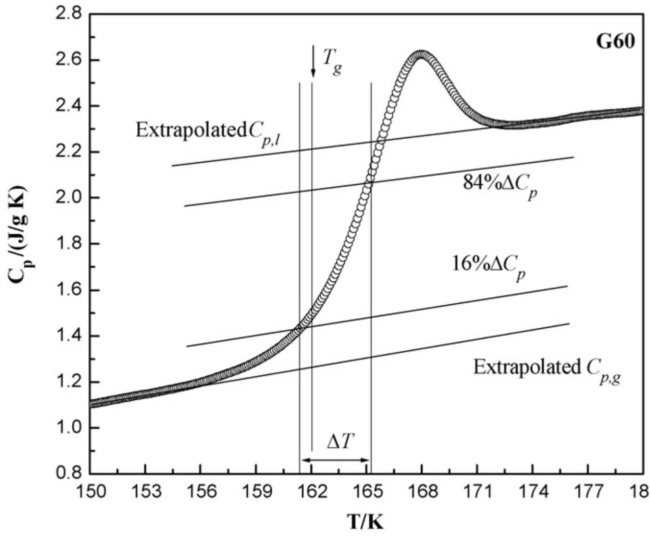

Fig. 3. Representative scheme for the determination of the temperature fluctuation in CRR.

NMR methods [27] are useful to investigate the length scale of the dynamic heterogeneities (ξ_{het}), which seems to be more direct than the calorimetry. Eq. (18) gives the size of an independently relaxing subsystem including all different subsets of particles. While NMR methods focus on a certain subset of all particles (for instance the less mobile particles). Hence the length scale of the CRR should be seen as the upper limit of the length scale of heterogeneities. As noted by the authors [11], NMR experiments carried out on glycerol [11] near T_g produced consistent results with the value obtained using Donth's formula ($\xi_{\mathrm{het}} = 2.9$ nm) [14]. According to Eq. (18), one can get the expression of the number of molecules included in the CRR:

$$N_{\mathrm{CRR}} = \frac{R T_g^2 \Delta C_p(T_g)}{\bar{C}_p^2 \delta T^2 M_s} \tag{19}$$

For PVAc, it shows that the size of CRR calculated using AG theory is within an order of magnitude of that obtained using Donth' method [28]. But Eq. (19) yields $N_{\mathrm{CRR}} = 598$ for glycerol. Thus, it seems to be no possibility to reconcile N_{CRR} with z^* in AG sense.

For pure glycerol, as discussion above, z^* obtained using Johari's formula is somewhat reasonable according to it physical meaning, while N_{CRR} in Donth's sense also seems to be reasonable according to Δh^*, β analysis and NMR measurement. The question is how to reconcile the big difference between 3.54 and 598. One possible solution is that z^* can only be used to describe the CRRs in some polymers other than the molecular H-bond liquids, even less their mixtures. So it is no possibility and unnecessary to reconcile these two parameters each other in the molecular H-bond liquids. Alternatively, a new physical meaning should be given to z^* in molecular H-bond liquids. Ngai [29] interpreted z^* in a new way as related to the primitive relaxation in the coupling model, not the cooperativity of the whole alpha relaxation. But this coupling model cannot reconcile the big difference raised above. It seems to be no possibility to resolve this problem using DSC method and the cooperativity of the alpha process in nonpolymeric glasses remain unanswered.

4. Concluding remarks

The AG equation together with the TNM model can be used reproduce the DSC structural relaxation behavior of glycerol and its aqueous solutions. Some of the model parameters and the structure relaxation time show a smooth dependence on the composition of the blend. In terms of the curve-fitting results, it can be concluded that conventional AG theory cannot 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 in the present systems.

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