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Comment on "Experimental evidence for excess entropy discontinuities in glass-forming solutions" [J. Chem. Phys. 136, 074515 (2012)]

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Lienhard *et al.*[1] report that the difference between the molar excess mixing entropies of supercooled 3- and 4-component liquids, ΔS^{l}_{mix}, and glasses, ΔS^{g}_{mix}, might not be zero at the glass transition temperature, T_g. The authors (i) measure the T_g and heat capacity change ΔC_p of bulk and emulsified 2-, 3-, and 4-component solutions using differential scanning calorimetry (DSC) and (ii) calculate the T_g of 3- and 4-component solutions using two approaches from Refs. 8 and 28 cited in Ref. 1. The difference between the calculated and measured T_gs is accounted for by ΔS^{l}_{mix}-$\Delta S^{g}_{mix} \neq 0$.[1] However, although the authors promise "Experimental evidence…" they do not present thermograms from which their data are extracted. Neither do they give sufficient information about the materials and experimental procedure used. This complicates reproduction of their results and verification of the validity of the conclusion on entropy excess discontinuity, which essentially states that the glass transition is a first order transition, a notion which goes against the current view of glass transition as a dynamic phenomenon.[2] In this Comment, we show that our T_g- and ΔC_p-data, including a quasi-invariant point,[3] (C'_g,T'_g), of aqueous citric acid (CA) differ from those reported in Ref. 1.

We measured bulk (~5.5 mg) and emulsified (~20-30 mg) CA/H$_2$O solutions of a concentration up to ~63.5 wt.% CA between 278 and 133 K using Mettler Toledo DSC 822. We employed an emulsification procedure and a matrix of 77 wt.% mineral-oil[4] + 23 wt.% lanolin (thereafter the ML-matrix) similar to that used in Ref. 1 in order to reproduce the results of Lienhard *et al.*. We also used a matrix of 80 wt.% halocarbon-oil+20 wt.% lanolin, (HL-matrix),[5,6] which produces a straight baseline between 278 and 133 K[7] and therefore does not perturb the T_g and ΔC_p of emulsified solutions. The droplet diameter in emulsions was ~0.5–30 μm. More information about our measurement technique is given elsewhere.[5,6] We employed a cooling/warming rate (3 K/min) lower than the 10 K/min used in Ref. 1. Earlier we showed[5,6] that the T_g of a freeze-concentrated solution (FCS) observed at 3 K/min is similar to that observed at the atmospheric temperature change of ~2 K/h. However, it is unclear whether this is the case for 10 K/min (600 K/h) used in Ref. 1. The fact that our ice melting temperatures, T_ms, are similar to those reported in Ref. 1 indicates that solution concentrations are similar in both studies. The origins of the inconsistencies between our and Lienhard *et al.*'s results are discussed below.

(i) ML-matrix or HL-matrix: Fig. 1(a) demonstrates that the ML-matrix vitrifies at $T_g^{ML} \approx 176.3$ K. The T_g^{ML} is similar to the $T_g \approx 176.5$ K of 55 wt.% CA droplets embedded into the ML- and HL-matrix, (Figs. 1(a) and 1(b)), and the $T_g \approx 176.6$ K of 55 wt.% CA reported in Ref. 1. This similarity indicates that: (a) there is no effect of the ML-matrix on T_g for the case $T_g \approx T_g^{ML}$, (b) the mineral oil used in this work and Ref. 1 is the same (see Ref. 4). However, the ML-matrix perturbs the ΔC_p of 55 wt.% CA droplets because it includes the ΔC_p^{ML} of the ML-matrix which is about twice as large as the ΔC_p of droplets. Further, the 60 wt.% CA thermogram demonstrates that the ML-matrix perturbs T_gs which are in the *vicinity* of the T_g^{ML}. The perturbed $T_g \approx 187$ K is ~7 K warmer than the unperturbed $T_g \approx 180$ K of 60 wt.% CA droplets in the HL-matrix, Fig. 1(b). Our *bulk* 60 wt.% CA also produces $T_g \approx 180$ K (not displayed) which is ~3 K colder than that of 60.1 wt.% CA in Ref. 1. Thus, the ML-matrix perturbs ΔC_p when $T_g \approx T_g^{ML}$ and T_g when it is in the vicinity of the T_g^{ML}.

(ii) Assignment of T'_g: As diluted solutions are cooled, the maximum freeze concentration, C'_g, and, consequently, the glass transition temperature of the *maximally* FCS, T'_g, are constant and independent of the initial solution concentration[3,6] and can be reached at an infinitely slow cooling rate.[8] In Ref. 1, the authors report only about the $T'_g = 214.3$ K and $T'_g = 218.8$ K of emulsified 20.4 and 50.1 wt.% CA.[1] However, the fact that these temperatures differ from each other by 4.5 K and the experimental accuracy is ±0.9 K[1] suggests that they are not true T'_g. This is confirmed by our thermograms displayed in Fig. 1(c) which show that only 20 wt.% CA droplets in the HL-matrix produce a subtle glass transition at ~206 K. The thermogram of 20 wt.% droplets in the ML-matrix shows no indication of a glass transition. 50 wt.% droplets embedded in both ML- and HL-matrixes also do not produce a glass transition but instead a double exothermic event at ~206 and 218 K which is not mentioned in Ref. 1. Thus, in contrast to what is

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stated in Ref. 1, the value of T'_g cannot be derived from emulsion experiments.

Yet, T'_g is derived from bulk experiments which reveal two thermal events, $T_1 \approx 204$ K and $T_2 \approx 218$ K, Fig. 1(d). The T_1 is close to the intersection point of the extrapolated T_g- and T_m-curves which define the quasi-invariant point, (C'_g, T'_g).[3,8] Our T_ms are similar to those reported in Ref. 1 only for concentrations up to 55 wt.% CA but colder by ~2 and 5 K for 60 and 63 wt.% CA (not shown). Also our T_g of 63 wt.% CA is ~3 K colder than that in Ref. 1. Using our T_m- and T_g-values, the extrapolated T_m- and T_g-curves intersect between ~203 and 205 K that is similar to $T'_g \approx 205$ K reported in Ref. 9.

(iii) Experimental procedure: The authors report the T_gs of bulk 70.2 and 75 wt.% CA and emulsified 70 and 75 wt.% MA (malonic acid). The solubility limit of CA is ~62 wt.% at 298 K[10] and that of MA is not known. The authors provide neither information on the temperature at which the concentrated solutions were prepared and then loaded into the calorimeter, nor on the temperature region of the measurements. Our experiments with such solutions prepared at ~85°C show that MA crystallizes during emulsion preparation, (Fig. 1(e)), and CA crystallizes upon cooling both at 3 and 10 K/min (not shown). We therefore believe that the T_gs reported in Ref. 1 are perturbed by the crystallization of solute (not only CA). The MA-crystallization together with the ML-matrix (see above) can be responsible for the non-monotonous behavior of the T_g of MA/H_2O in Ref. 1.

(iv) Uncertainty of ΔS^{l}_{mix}-ΔS^{g}_{mix}: The authors do not present its value. Their Eq. (12) shows that the values and uncertainty of ΔS^{l}_{mix}-ΔS^{g}_{mix} depend mainly on the $\Delta C_p^{W} = c_1^{\,l} - c_1^{\,g}$ of water and weakly depend on the scattering of experimental T_gs. From extrapolation in a dilution series in Fig. 3(c) in Ref. 1 they determine a ΔC_p^{W} of 34 J mol^{-1} K^{-1}, which is much larger than the ΔC_p^{W} of ~0.7 J mol^{-1} K^{-1} measured directly on glassy water samples.[11] Also when using the approach of extrapolating to zero concentration, we arrive at a much lower value of the ΔC_p^{W} of 18 J mol^{-1} K^{-1} from the data in Fig. 3(c) in Ref. 1. Using this latter value instead of 34 J mol^{-1} K^{-1} we find a deviation of 7.4 J mol^{-1} K^{-1} from the ΔS^{l}_{mix}-$\Delta S^{g}_{mix} \approx 4$ J mol^{-1} K^{-1} reported for 60.1 wt.% CA in Fig. 4 in Ref. 1 and an even a much larger deviation when using the directly measured ΔC_p^{W}. Based on this uncertainty in ΔC_p^{W} it cannot be decided whether the ΔS^{l}_{mix}-ΔS^{g}_{mix} difference is zero or different from zero using the approach presented by Lienhard *et al.*

In conclusion, the material presented in this Comment shows that T_g and c^{l}–c^{g} data reported in Ref. 1 for the CA/H_2O are not persuasive, which casts doubt on the validity of their estimation of ΔS^{l}_{mix}-ΔS^{g}_{mix}. The thermograms presented here do not require evocation of a discontinuity in entropy at the glass transition, but are in agreement with the glass transition representing a continuous slow-down of dynamics and continuous change in entropy.

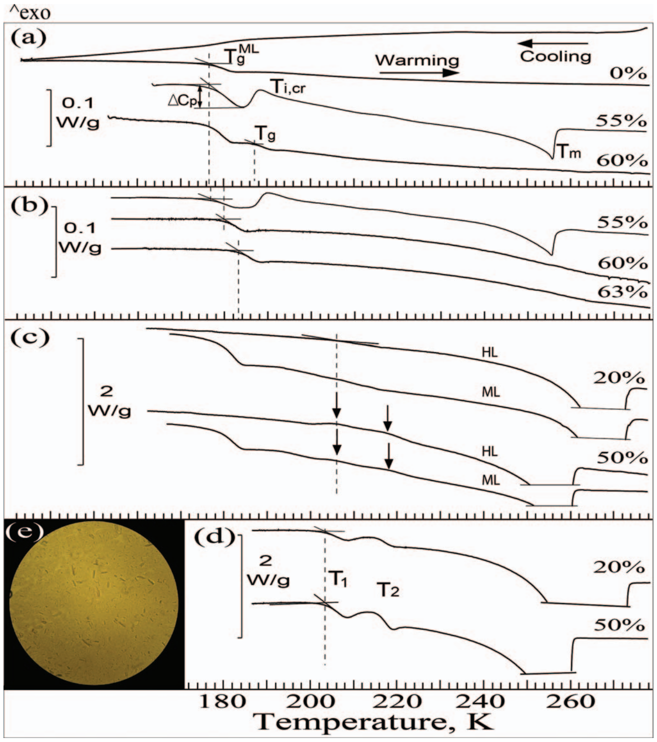

FIG. 1. (a) Cooling and warming thermograms of ML-matrix (0 wt.% CA) and only warming thermograms (shown for clarity) of emulsified CA/H_2O droplets embedded into ML-matrix. (b) Thermograms of emulsified droplets embedded into HL-matrix. (c) Thermograms of emulsified 20 and 50 wt.% CA droplets embedded into ML- and HL-matrices. Arrows mark a double exothermic event. (d) Thermograms of bulk CA/H_2O samples. (e) Optical microscope picture of emulsified 70 wt.% MA before measurement. Diameter of the droplets is less than ~3 μm and the size of MA-crystals less than ~15 μm. Glass transition temperatures, T_g, are determined as the intersection of a baseline and a line drawn along a step of heat capacity change, ΔC_p. $T_{i,cr}$ marks the crystallization of ice upon warming and T_1 and T_2 the two thermal events of (M)FCS (see text). The skewed lines truncate ice melting peaks, T_m, to fit the figure. The concentration of samples is indicated. Scale bars denote heat flow through samples.

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[4] Lienhard *et al.*[1] did not report about the mineral-oil used. T. Koop, a co-author of Ref. 8 in Ref. 1, informed us that they used a mineral-oil with CAS number 8042-47-5 (Aldrich). Since D. Lienhard belongs to the same scientific group, we believe that he used the same mineral oil.

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