

Response to “Comment on ‘Experimental evidence for excess entropy discontinuities in glass-forming solutions’” [J. Chem. Phys. 139, 047101 (2013)]

Daniel M. Lienhard, Bernhard Zobrist, Andreas Zuend, Ulrich K. Krieger, and Thomas Peter

Citation: *J. Chem. Phys.* **139**, 047102 (2013); doi: 10.1063/1.4812930

View online: <http://dx.doi.org/10.1063/1.4812930>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v139/i4>

Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



www.goodfellowusa.com

Goodfellow

metals • ceramics • polymers • composites

70,000 products

450 different materials

small quantities *fast*

Response to “Comment on ‘Experimental evidence for excess entropy discontinuities in glass-forming solutions’” [J. Chem. Phys. 139, 047101 (2013)]

Daniel M. Lienhard,^{1,a)} Bernhard Zobrist,^{1,2} Andreas Zuend,³ Ulrich K. Krieger,¹ and Thomas Peter¹

¹*Institute for Atmospheric and Climate Science (IAC), ETH Zurich, Zurich, Switzerland*

²*Faculty of Chemistry, Bielefeld University, Bielefeld, Germany*

³*Department of Chemical Engineering, California Institute of Technology, Pasadena, California 91125, USA*

(Received 15 March 2013; accepted 20 June 2013; published online 23 July 2013)

[<http://dx.doi.org/10.1063/1.4812930>]

In their comment, Bogdan and Loerting¹ (hereafter called BoLo) question the validity of the experimental data of Lienhard *et al.*² (hereafter called LZZKP) concerning the glass transition temperatures (T_g) of binary aqueous citric acid and aqueous malonic acid solutions. BoLo present own measurements and find disagreements between their results and the results published by LZZKP. In this reply, we show calorimetric thermograms from which the results published by LZZKP are derived and discuss why BoLo’s criticisms are unjustified. Below, we address each of the four claims.¹

(i) Mineral-oil/lanolin vs. halocarbon-oil/lanolin as emulsion matrix: BoLo question the validity of the emulsion data reported in LZZKP because the mineral-oil/lanolin (mineral-oil CAS number 8042-47-5) mixture which is used forms itself a glass around 177 K, here referred to as T_g^m . The mineral-oil/lanolin mixture was used by LZZKP because of the high reproducibility experienced in previous studies.^{3–5} Indeed, T_g^m appears in each emulsion experiment at ~ 177 K, but this matrix glass transition can easily be distinguished from the glass transition of the emulsified aqueous droplets. The heating cycles shown in Fig. 1(a) for emulsified aqueous malonic acid droplets clearly reveal the two distinct glass transitions. The experiment with a malonic acid weight fraction (w_2) of 0.565 shows crystallization upon warming, the thermal signature of which superimposes the glass transition of the mineral-oil/lanolin matrix. We further show the heating cycles of emulsified aqueous NH_4HSO_4 droplets reported in Ref. 5, which were also used by LZZKP in Fig. 1(b).

The emulsion experiment with a citric acid weight fraction of 0.550 in Fig. 1(c) shows only one glass transition upon cooling, although both the mineral-oil/lanolin matrix and the aqueous droplets vitrify. The reverse transition (glass to supercooled liquid) occurs in the heating cycle followed by cold crystallization and was interpreted as T_g of the aqueous droplets, which in this experiment coincides with T_g^m . We note that this T_g is in good agreement with the predicted T_g based on our bulk measurements.

BoLo’s emulsion measurements with a halocarbon-oil/lanolin matrix and their bulk measurements yield a T_g which is 3 K lower than ours, which is not surprising as T_g de-

pends on the cooling rate of the experiment, with larger cooling rates leading to higher T_g .⁶ They used a cooling rate of 3 K/min, whereas we applied the widely used cooling rate of 10 K/min.⁷ One order of magnitude reduction in the cooling rate typically lowers T_g by 3–5 K.⁸ In fact, when this difference is taken into account, the bulk measurements of BoLo agree with those from LZZKP within the experimental uncertainty. This interpretation of BoLo’s results reduces the inconsistencies to a single experiment, namely, the one with aqueous droplets containing a citric acid weight fraction of 0.6 embedded in a mineral-oil/lanolin. However, we believe that the T_g -curve in Fig. 1 of LZZKP, which is based on a series of unambiguous bulk measurements, is much more convincing than this single experiment of BoLo. For comparison, we included BoLo’s measurements in the phase diagram of the citric acid-water system (see supplementary material¹⁸).

(ii) Assignment of T'_g : BoLo raise doubt about the glass transition temperature of the freeze-concentrated citric acid solution, T'_g , reported by LZZKP. They suspect that the reported T'_g (for which the uncertainty is higher than for T_g because the change in the heat flow due to this transition is weak) were confused with the signal from the termination of ice crystallization in the heating cycle. However, such a termination of ice crystallization in the heating cycle implies that the same crystallization must have been kinetically hindered in the cooling cycle. This kinetic limitation is conceivable but unexpected in emulsion experiments because the distance that the water molecules need to travel in the emulsified aqueous droplets is very small. It is therefore not surprising that our results agree with values found by Lu and Zograf⁹ who investigated annealed samples in a procedure recommended for the determination of T'_g .¹⁰ In agreement with the study of Lu and Zograf,⁹ we found two heat flow discontinuities upon heating, T'_{g1} and T'_{g2} , shown in the inset of Fig. 1(c). The higher one (T'_{g2}) was assigned to the actual T'_g , while the lower (T'_{g1}) was interpreted as the glass transition of droplets where ice did not reach equilibrium size.⁹ However, there are different interpretations of such discontinuities upon heating.^{11–15} It is possible that T'_{g1} is the actual T'_g , and T'_{g2} corresponds to the onset point of melting, usually referred to as T'_m .^{14,15} We do agree with BoLo that there is uncertainty concerning this attribution. However, we would like to underline that the value of T'_g is irrelevant for the conclusions drawn by LZZKP.

^{a)}Electronic mail: daniel.lienhard@env.ethz.ch

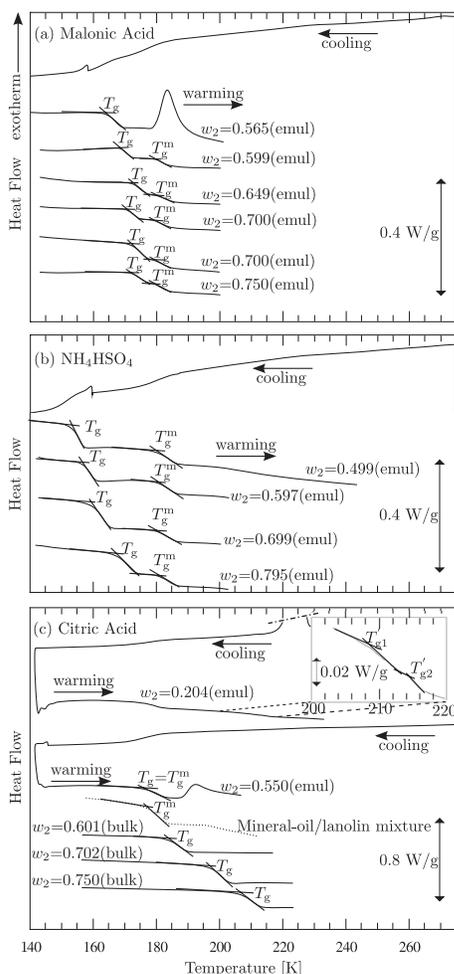


FIG. 1. Calorimetric thermograms of bulk and emulsified aqueous solutions containing (a) malonic acid, (b) NH_4HSO_4 , and (c) citric acid, which are exemplary for the data reported by LZZKP (citric acid and malonic acid) and Zobrist *et al.*⁵ (NH_4HSO_4). Concentrations and technique (bulk or emulsion) are indicated. The tilted dashed-dotted line in panel (c) truncates the freezing peak to fit the figure. The scale bars represent heat flow through samples. The dotted line in panel (c) shows the warming cycle of the mineral-oil/lanolin mixture in the absence emulsified droplets.

(iii) Experimental procedure: BoLo report that they could not reproduce the T_g of bulk aqueous citric acid solutions with citric acid weight fractions of 0.70 and 0.75. When we prepared these solutions, we took care that no impurities that may provide surfaces for heterogeneous nucleation entered the vial during the preparation. For the same reason, we did not use stir bars and held the temperature of the solution above its solubility for some time to ensure that no undissolved citric acid crystals invisible to the eye were left in the solution. It is not unusual that aqueous solutions can be supercooled with respect to the solid phase of the solute. Both Refs. 9 and 16 observed T_g of aqueous citric acid solutions with $w_2 > 0.70$. The calorimetric thermograms of the relevant aqueous citric acid solutions observed from both bulk and emulsified samples reported by LZZKP are displayed in Fig. 1(c).

The same procedure was applied for the aqueous malonic acid solutions. Additionally, as described by LZZKP, the emulsified aqueous malonic acid droplets with $w_2 = 0.750$ were heated to the melting temperature of pure malonic acid

after T_g was observed, to make sure that no crystal was formed in the cooling cycle (not shown).

(iv) Uncertainty of $\Delta S_{\text{mix}}^l - \Delta S_{\text{mix}}^g$: BoLo dispute the choice of $c_1^l - c_1^g$ and criticize the absence of an uncertainty estimation for $\Delta S_{\text{mix}}^l - \Delta S_{\text{mix}}^g$. First, we would like to clarify that $c_1^l - c_1^g$ denotes the heat capacity difference between liquid and the glassy state of water at $T_g = 136$ K of pure water. As pure water undergoes a fragile-to-strong transition, which is suppressed in the presence of a solute, the value of $c_1^l - c_1^g$ depends on how pronounced this conversion is, even when the solute is absent at $w_2 = 0$. Therefore, $c_1^l - c_1^g$ needs to be evaluated for each solute individually, as shown by LZZKP. We believe that the description provided by LZZKP and the references cited therein^{15,17} fully justify the procedure. Second, as a consequence of Eq. (12) of LZZKP, the value of $c_1^l - c_1^g$ only scales the value of $\Delta S_{\text{mix}}^l - \Delta S_{\text{mix}}^g$ for each individual solute, but has no effect on the relative quantities between the different solute concentrations. Regardless of the uncertainty in $c_1^l - c_1^g$, which ranges from 12 to $35 \text{ J K}^{-1} \text{ mol}^{-1}$, $\Delta S_{\text{mix}}^l - \Delta S_{\text{mix}}^g$ must adopt non-zero values. This is why no error bars are provided for $\Delta S_{\text{mix}}^l - \Delta S_{\text{mix}}^g$.

(v) Classification of the glass transition: In addition to points (i) to (iv), BoLo state that the entropy excess discontinuities found by LZZKP imply that the glass transition is a first order transition. However, our work does not warrant such a conclusion. The data and evaluation with regard to the excess entropy discontinuity suggest only that the glass transition is not a classical second order phase transition according to the Ehrenfest classification. Additionally, the shape of the heat flow curves at the glass transition indicates that the transition is not a first order transition. Note that the glass transition occurs between two metastable states (supercooled liquid to amorphous solid) and is at least partially a dynamic phenomenon, hence the transition temperature depends on the cooling rate.⁶ Therefore, it is not a purely thermodynamically controlled phase transition, which complicates the classification according to Ehrenfest.

To summarize, we thank BoLo for a series of new measurements, which, as far as the conclusions of LZZKP are concerned, corroborate our findings. The ETH Research Grant ETH-0210-1 is acknowledged.

- ¹A. Bogdan and T. Loerting, *J. Chem. Phys.* **139**, 047101 (2013).
- ²D. M. Lienhard *et al.*, *J. Chem. Phys.* **136**, 074515 (2012).
- ³B. Zobrist *et al.*, *Atmos. Chem. Phys.* **6**, 3115 (2006).
- ⁴C. Marcolli *et al.*, *Atmos. Chem. Phys.* **7**, 5081 (2007).
- ⁵B. Zobrist *et al.*, *Atmos. Chem. Phys.* **8**, 5221 (2008).
- ⁶P. G. Debenedetti and F. H. Stillinger, *Nature (London)* **410**, 259 (2001).
- ⁷C. A. Angell, *Chem. Rev.* **102**, 2627 (2002).
- ⁸M. D. Ediger *et al.*, *J. Phys. Chem.* **100**, 13200 (1996).
- ⁹Q. Lu and G. Zografis, *J. Pharm. Sci.* **86**, 1374 (1997).
- ¹⁰Y. H. Roos, *Carbohydr. Res.* **238**, 39 (1993).
- ¹¹H. Levine and L. Slade, *Carbohydr. Polym.* **6**, 213 (1986).
- ¹²Y. H. Roos and M. Karel, *J. Food. Sci.* **56**, 266 (1991).
- ¹³E. Y. Shalaev and A. N. Kanev, *Cryobiology* **31**, 374 (1994).
- ¹⁴Y. H. Roos, "Phase transitions and transformations in food systems," in *Handbook of Food Engineering* (CRC Press, Boca Raton, 2007).
- ¹⁵H. R. Corti *et al.*, *Pure Appl. Chem.* **82**, 1065 (2010).
- ¹⁶E. Maltini, M. Anese, and I. Shtylla, *CryoLetters* **18**, 263 (1997).
- ¹⁷H. R. Corti *et al.*, *Phys. Chem. Chem. Phys.* **13**, 19741 (2011).
- ¹⁸See supplementary material at <http://dx.doi.org/10.1063/1.4812930> for phase diagram of the citric acid-water system as a function of the citric acid weight fraction as in LZZKP.