

Report on Doctoral Thesis:

The role of entropy in the description of relaxation dynamics of ionic liquids

by

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The doctoral thesis of Mr. Shinian Cheng addresses the subject of a relationship between dynamical and thermodynamical properties of ionic liquids. The thesis is based on four papers with Mr. Cheng as the first author – two of the works were published in *Journal of Chemical Physics*, one in *Journal of Molecular Liquids* and one in *Journal of Physical Chemistry B*.

The papers (attached to the thesis) are preceded with an overview including a short description of basic properties of ionic liquids and four other sections on which I will comment below. The description is carefully thought out and informative, although, personally I would appreciate a more elaborated introduction. I would also suggest to modify the terminology (this is hardly possible in this thesis, but would be useful in future) – the scientific community investigating glass transition phenomena often use the term “*good glass-formers*” that does not have a well-defined meaning; the terminology is used more often in the thesis. Analogously, some of the sentences, such as: “*Similar to molecular liquids, the lower limit of a liquid range of ionic liquids belongs to the solid-liquid transition...*” are not clear.

In the next section of the overview, molecular (ionic) dynamics effects characteristic of the glass transition region are outlined. The section also addresses the subject of entropy and enthalpy changes upon glass transition. The great advantage of this section is the comprehensive literature summary (the same applies to the next section). The thesis includes a thorough and extensive overview of literature and, in this way, it can serve as an excellent material introducing the Reader to the subject of dynamics and thermodynamics of glass forming liquids. However, to somewhat equilibrate the enthusiasm, I see some “weaker points” of this section. The most important one is the lack of a precise (or even less precise) definition of “relaxation dynamics”. Explanation of the mechanism of the, so called, “relaxation dynamics” is essential for understanding the “scientific message” of the studies presented in the thesis. The Reader might wonder whether by “relaxation dynamics” one understands rotational dynamics of molecules (ions) or correlated (cooperative) reorientation, whether translation diffusion has something to do with the “relaxation dynamics” (after all conductivity is an important quantity considered in the studies and conductivity is related to translation diffusion). The sentence: “*As the temperature is changed, the molecules of a supercooled liquid will reach a new equilibrium*

state, namely, the structural relaxation process.” There is also the term “*strong liquids*” used, for instance, in the legend of figure 2.4, that similarly to “*good glass-formers*” does not offer much explanation (the terminology is explained only later).

In the next section, Mr. Cheng presents theoretical models linking entropy of glass forming systems (the section should be entitled: “*Models ...*” instead of “*Methods ...*”). The presentation is clear and comprehensive. One might note that there are simpler ways to explain the concept of the Kauzmann temperature – it would be sufficient to say that at that temperature the liquid entropy and the crystal entropy become equal (without referring at this stage to excess entropy). I have, however, some critical remarks regarding Section 4: *Experimental techniques and Materials*. I would appreciate a more elaborated description of the experimental methods – for instance when talking about Dielectric Spectroscopy and conductivity it should have been explained how to obtain the conductivity values from the experimental data (in terms of the physical mechanism and the mathematical formulae). Then, the section includes two tables that summarize some properties of the ionic liquids that have been used in the studies. The reason of grouping the liquids into two tables is not clear to me – what was the selection rule for including a liquid into Table 4.1 or Table 4.2? Moreover, why Table 1 is entitled: “*Detail information and chemical structures of examined samples*”, whereas Table 4.2 is entitled: “*The basic information and structures of the studied ILs*”. The information included into the two tables are the same (and they are basic). It would be useful to group the liquids in explicit connection to the papers.

In fact, one could say the same about Section 5 in which the results are presented – there are no references in this section to the publications on which the thesis is based and, hence, in which the results have been described.

Putting this criticism aside, I have to say that when it comes to the scientific outcome, I’m impressed by the work of Mr. Cheng. This is not only the matter of the four papers – Mr. Cheng is the author of ten more publications devoted to the subject of dynamical properties of ionic liquids. Mr. Cheng stated very modestly: “*In addition to the subject discussed in this dissertation, I have also been interested in several other relevant topics connected to ionic liquids and polymerized ionic liquids during my Ph. D studies.*” The point is that Mr. Cheng is the first author of three of these works – they are published in ACS Macro Lett., Phys. Chem. Chem. Phys. and Polymer. In addition, there is no doubt that the contribution of Mr. Cheng to the next seven publications is significant. This outcome shows that Mr. Cheng is an extraordinary, highly motivated scientists with deep expertise (already at the early stage of his scientific carrier that, I hope, he will continue) in dynamical and thermodynamical properties of condensed matter systems.

Coming back to the subjects of the four papers being the basis of the thesis, one can summarize them as follows:

Testing the Adam-Gibbs model: Shear viscosity and conductivity of selected ionic liquids were measured in a broad temperature range (ensuring changes in the conductivity by more than ten decades). Then the temperature dependences of these quantities were analyzed in terms of the Vogel-Fulcher-Tammann equation. On the other hand configurational and excess entropy was calculated versus temperature on the basis of calorimetric data. By merging the entropy with viscosity and conductivity the Adam-Gibbs model was verified and, to some extent, questioned (in some cases the model failed). In the course of these studies it has been found that the temperature dependencies of viscosity can be reproduced in terms of a single Vogel-Fulcher-Tammann term in contrast to most low-molecular van der Waals liquids for which a superposition of two Vogel-Fulcher-Tammann terms are needed. A next finding concerns the temperature evolution of conductivity that clearly shows a crossover from a non-linear to linear behavior – the deviations from the linearity were explained by calculating isobaric fragility of the systems. A next category of findings concerns entropy. It was shown that the approximated equality of configurational and excess entropy does not hold for the investigated ionic liquids, especially at higher temperatures. As a consequence, it turned out that one can hardly determine a single Kauzmann temperature for these systems. Moreover, it was shown that a relationship between glass transition temperature and Kauzmann temperature established for molecular glass-forming systems does not apply to ionic liquids.

Exploiting the thermodynamic scaling concept: The thermodynamic scaling was applied to conductivity versus volume. It was shown that the scaling exponent of conductivity is state-independent. Analogously, the concept was exploited for entropy versus density. It turned out that the scaling exponent is a linear function of entropy. In the course of the studies it was shown that conductivity scaled versus a product of temperature and volume with a constant scaling exponent forms an universal curve covering thirteen orders of magnitude of the conductivity changes.

One could continue with outlining the results, but this is not the main purpose of this report. The outline is meant to show that Mr. Cheng addressed in his thesis scientific problems with a high level of novelty and that the studies required a combination of experimental expertise and a deep knowledge of the theoretical models linking dynamical and thermodynamical properties of glass-forming systems. Mr. Cheng attached to his thesis declarations of co-authors regarding their contributions to the individual publications and his own declarations. Not going into details, it is sufficient to say that Mr. Cheng indeed played the main role in these works – the statement: “*I conceived the study, planned and carried out the experiments, analyzed the experimental data, discussed the results, prepared the figures, and wrote the manuscript*” is self-explaining.

The results are described in Section 5. The advantage of the section is the description of the methodology of the data analysis that led to establishing the relationships between the dynamical and thermodynamical quantities. Personally, I would appreciate a more elaborated conclusion section including the main findings; the Summary section is too short to underline the essential results.

Summarizing, I state that the doctoral thesis of Mr. Shinian Cheng entitled " The role of entropy in the description of relaxation dynamics of ionic liquids" meets the conditions set out in the Act of March 14, 2003 on scientific degrees and scientific title as well as degrees and title in the field of art (Journal of Laws No. 65, item 595, as amended) . Consequently, I postulate to proceed to further stages of the procedure. Moreover, I propose to consider the thesis for distinction in the light of its high scientific merit.



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