

Quantum simulations of lithium ion solvation dynamics in mixed Stockmayer clusters

Quantum thermodynamic simulations are carried out for three Stockmayer clusters modeling a typical lithium ion battery electrolyte. The ionic cluster contains a lithium ion solvated by six strong dipoles and twelve weaker ones. The parameters of the interactions are tuned to reproduce bulk properties of nitromethane and tetrahydrofuran (THF) for the strongest, resp. weaker dipolar solvent molecules. The physical properties of the ionic cluster are compared with those of the related neutral and solvent mixture systems. We find that the quantum effects for the solvated lithium ion are significant at room temperature and several degrees above it. In Fig. 1 the classical (white circles) and quantum (black circles) heat capacities for the three systems and the solvation energy are compared. The quantum calculations are carried out with a cubically convergent Fourier Path Integral adapted for computations in curved spaces. Inspections of the properties of interest for several Fourier coefficients confirms that convergence is reached with 8 coefficients at 80 K and above for all three systems. We display the properties in Fig. 1 over a smaller range of temperatures to emphasize several critical features. Firstly, the systems clearly approach classical behavior at the high end of the temperature range. The data in graph (b) of Fig. 1 demonstrates that the cluster with neutral Li approaches classical behavior around 175 K, whereas the solvent cluster in graph (c) proves to behave classically at temperatures as low as 80 K. These temperatures are in stark contrast when compared to those in graph (a) and (d) where the quantum effects of the solvated lithium persist at much higher temperatures. The quantum effects are still significant, albeit small, at 360 K for the heat capacity and 300 K for the solvation energy. Additionally, the main features of the three heat capacities are not shifted to lower temperatures suggesting that the melting of the cluster is not affected by quantum fluctuations.

By comparing the quantum and classical behavior of the two solvated lithium species we can conclude that the quantum effects are attributable to a) the relative small mass of the ^7Li nucleus, and b) the strong interactions between the ion and the nitromethane molecules. Structural data suggest that the nitromethane-like dipoles remain bound to the ion at temperatures above the melting range of the THF layer. While the model we have used in the present study is coarse grained, we expect the quantum effects to be comparable to those computed with a more realistic model, since the classical behavior of the solvent at and above 80 K is the result of the total masses and the relatively large moments of inertia rather than the details of the interactions. Therefore, the conclusions regarding the nuclear quantum effects are likely to be useful to the community of investigators who employ simulations to provide insights into the relation between molecular structure and performance of the electrolyte solution, at the electrode-electrolyte interface, and to suggest ways to design novel electrolytes to name a few important applications involving lithium ions. With these results one can assume that the majority of the nuclear quantum effects in such future simulations can be accounted for simply by treating the ^7Li nucleus as a quantum object and the solvent by classical mechanics.

The data in Figs. 1 suggests that one can simply use one time slice (or coefficient) for the solvent molecules, essentially treating them as classical objects, and as many as necessary for the solute. This particular feature should make the determination of the ^7Li nuclear quantum effects feasible in much larger systems and with more sophisticated potentials than we do here. We test the idea and find that the agreement between the heat capacity above 80K between the results of the mixed classical quantum simulations and those where the full clusters is treated quantum mechanically are not in agreement quantitatively at any temperature, suggesting that the first solvation layer should be treated quantum

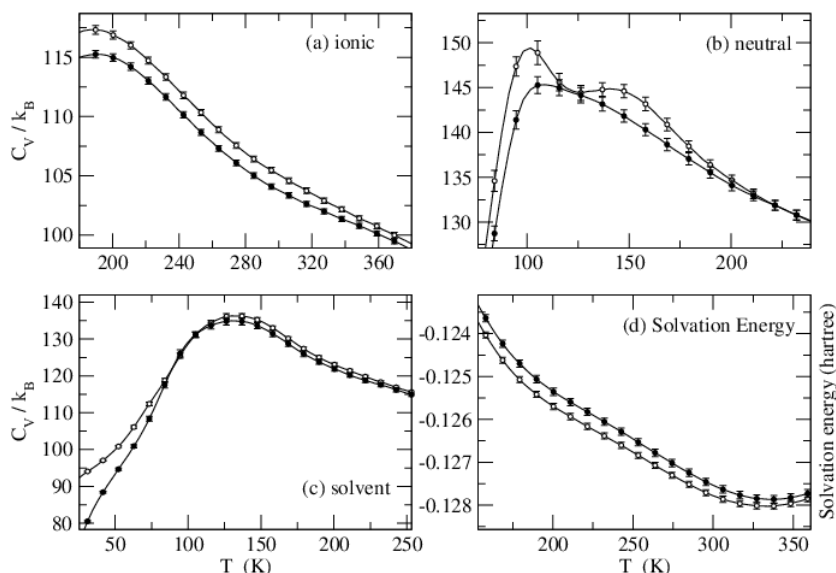


FIG. 1. Classical (white circles) and quantum results (black circles) are compared. (a) The heat capacity in units of the Boltzmann constant for a lithium ion solvated by six nitromethane and twelve THF like Stockmayer particles. (b) Same as (a) but with a neutral lithium atom. (c) The same property for the eighteen dipoles. (d) The solvation energy for Li^+ in hartree.

Mechanically as well. More work is needed to establish an accurate subdivision between the quantum and the classical domains. We explore how nuclear quantum effects impact the ^7Li ion transport and solvation dynamics by developing strategies to perform these types of quantum simulations. Among those investigated are Ring Polymer Molecular Dynamics (RPMD) simulations, and we have developed two different approaches. The first approach is an adaptation of the RPMD for curved spaces we have developed a few years ago. In this approach, a set of starting positions and momenta are obtained by converting an equilibrated Fourier Path Integral simulations into the corresponding path configurations. The second is a development of the real time dynamics directly from the Fourier Path integral. The latter method, when coupled with a cubically convergent algorithm could retain the same convergence advantage when dynamic properties are simulated. These efforts are ongoing at the time of this writing.

Finally, the systems we have investigated in this work are too small to determine if $^7\text{Li}^+$ is predominantly in the core of a sufficiently large cluster in the liquid state. Though the ion is solvated by one layer of nitromethane dipole, there are insufficient THF - like particles to produce a less asymmetric liquid second solvation layer. We hypothesize that the number of solvent dipoles needed to create a more symmetric solvent nanodroplet should not be much bigger than what we have already simulated. To test this idea we have investigated a system that models a lithium ion solvated by six nitromethane molecules and one hundred THF - like dipoles. While this larger clusters is not equivalent to a bulk electrolyte; e.g. there are no counter-ions, no periodic boundary conditions, we find some familiar themes. (a) The classical heat capacity contains a single narrow dominating feature corresponding to the melting of the solvent. (b) The lithium ion - nitromethane subsystem is not comprised of six nitromethane molecules but five in the solid range and four at or near room temperature. (c) Just like the smaller systems, the lithium ion - nitromethane subsystem segregates from the rest of the solvent upon freezing, but the THF solvent engulfs the ion and its solvation layer. The establishment of the aforementioned separation between the quantum and the classical subsystems is especially critical. For a cluster of this size the cost of a full quantum treatment is prohibitive.

