

MONTE CARLO STUDY OF SOLID ELECTROLYTES

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A simple version for superionic conductors, of the soft-core model for simple liquids is proposed. That is, the model potential is composed of only the soft-core and Coulomb potentials. Monte Carlo simulations for two solid electrolytes, $\alpha\text{-AgI}$ and CaF_2 , are made with a fine-grained lattice for a 108-ion system and a 324- or 96-ion system, respectively, at several temperatures. For both systems we have observed sublattice disordering for an appropriate temperature range. We have obtained the partial pair distribution functions, one-body distribution of ions and mean-square displacement of ions as a function of the Monte Carlo time-step. Our results are satisfactorily compared with experimental findings and with molecular dynamics calculations. It is found for CaF_2 that as the temperature increases the fractional number of anions in the tetrahedral locations shows a drop in magnitude for a narrow temperature range, and that results obtained on the fluctuations of potential energies in the superionic phase present a rather large system-size-dependency.

1. Introduction

We propose a simple model system with ionic potentials consisting of only the soft-core and Coulomb potentials. Our model may be considered as a version for superionic conductors, of the soft-core model which has been successfully applied to simple liquids [1,2]. On the other hand, the recently proposed excluded-volume model [3] is simply a version of the hard-core model [4]. The present model will be useful for extracting a leading term of pair potentials relevant to the phenomena.

We carried out Monte Carlo calculations for two solid electrolytes, $\alpha\text{-AgI}$ and CaF_2 , using our model potential. In order to avoid the time-consuming calculation of the electrostatic energies (the Ewald sums) we used the fine-grained lattice model which is made by successive binary divisions of the unit cell, and which approximates a corresponding continuum system

very accurately [5]. This method enabled us to tabulate, in advance, potential energies for all possible distances on the lattice, and hence considerably reduce the computation time for the calculation of the potential energy. This method of calculation is, therefore, particularly useful for surveying various properties of the model as a function of temperature.

2. Model

We consider a model system with the following pair potential $\phi_{ij}(r)$ between any ions

$$\phi_{ij}(r) = A_{ij}[(\sigma_i + \sigma_j)/r]^n + Z_i Z_j e^2/r, \quad (1)$$

where i, j describe the types of ions; A_{ij} the repulsive strength; σ_i, σ_j the ion radii; Z_i, Z_j the fraction of charge. The present model is considerably simplified since both the polarization and dispersion energy terms are neglected in eq.

(1). We have used following values of the potential parameters. $\alpha\text{-AgI}$: $\sigma_+ = 0.63 \text{ \AA}$, $\sigma_- = 2.20 \text{ \AA}$, $|Z_+| = |Z_-| = 0.6$, $A_{ij} = A = 1.23 \times 10^{-2} \times e^2/\text{\AA}$ and $n = 7$. These are the same as those of Vashishta and Rahman [6]. The lattice constant, a , was 5.08 \AA . The calculation was made in a system of 54 cations and 54 anions initially forming a bcc structure (anions) with cations distributed over suitable tetrahedral sites. CaF_2 : For simplicity we assumed that $A_{ij} = A$ and $\sigma_+ = \sigma_- = \sigma$. The latter assumption was made as one of the most preferable conditions for which the sublattice disordering of anions is expected [7]. With lattice constant, $a = 5.90 \text{ \AA}$, σ_+ and σ_- were taken so that both ions contact in nearest-neighbor distance, i.e. $\sigma_+ = \sigma_- = (3^{1/2}/8)a = 1.28 \text{ \AA}$. The strength parameter A was fitted to the Kim-Gordon potential [8] at the nearest-neighbor distance; this yields $A = 1.07 \times 10^{-2} e^2/\text{\AA}$. We used $Z_+ = 2$, $Z_- = -1$ and $n = 12$. The choice for the value of n is based on the consideration in ref. [7]. The Monte Carlo calculations were performed on a 324-ion system and a 96-ion system initially forming a fluorite lattice.

3. Results

3.1. $\alpha\text{-AgI}$

The Monte Carlo simulations were performed at the temperatures $k_B T/A = 0.290, 0.387, 0.484, 0.581, 0.629, 0.678$ and 0.968 . The pair distribution function corresponding to anion pairs $g_{--}(r)$ at the lowest temperature of interest displays a structure similar to that of an fcc lattice, while the function at higher temperatures presents a rather broad main peak as observed in all bcc structures [8].

The pair distribution functions for $k_B T/A = 0.484$ show that the maxima of $g_{--}(r)$, $g_{++}(r)$ and $g_{+-}(r)$ occur at 4.3 \AA , 4.0 \AA and 2.8 \AA with heights of 3.2, 1.5 and 3.1. These values are in good agreement with those of Vashishta and Rahman [6].

The mean-square displacement generated from the MC process has revealed [8] that at

$k_B T/A = 0.290$ anions and cations are completely or almost non-diffusive, only cations become diffusive at $k_B T/A = 0.484$, and both ions become diffusive at $k_B T/A = 0.678$.

From one-body distribution of both ions, which are obtained by joining positions of ions averaged over 20 MC time-steps, it has also been shown [8] that anions form a stable regular arrangement at $k_B T/A = 0.290$ and 0.484 , but at $k_B T/A = 0.678$ the arrangement becomes relatively disordered. At $k_B T/A = 0.290$ cations appear to remain almost in localized regions, whereas cations at $k_B T/A = 0.484$ are seen to move over a distance comparable with the neighboring distance of the anion sublattice.

The phase change from the superionic to the normal crystalline phase is predicted to occur around $k_B T/A \approx 0.35$, accompanying the structural transition of the anion sublattice (bcc to fcc-like structure), and from the superionic to the liquid phase around $k_B T/A \approx 0.65$. It follows that the temperature range of the superionic phase T_m (melting)/ T_s (superionic transition) is predicted to be ≈ 1.86 , a value very close to the experimental value (1.98) for $\alpha\text{-AgI}$. The absolute temperature is, however, about 1.5 times higher than that found for $\alpha\text{-AgI}$. This discrepancy is overcome if one uses a reduced value of A .

The time variations of x , y , and z -coordinates of cations has shown [8] that cations spend the vast majority of their time around tetrahedral sites (0, 1/4, 1/2), a rather large amplitude showing high anharmonicity ($k_B T/A = 0.484$). This result supports the predictions on the cation density distribution for $\alpha\text{-AgI}$ by Hoshino et al. [9], Cava et al. [10], and Vashishta and Rahman [6].

3.2. CaF_2

The pair distribution function for $k_B T/A = 1.949$ are found to agree quantitatively with those of Rahman [11]; in the results of the latter the maxima of $g_{++}(r)$, $g_{--}(r)$ and $g_{+-}(r)$ occur at 4.0 \AA , 2.9 \AA and 2.2 \AA with the heights 3.2, 1.9 and 4.2, respectively, and in the present work the maxima occur at 4.0 \AA , 2.9 \AA and

2.3 Å with the heights 3.1, 1.7 and 4.2, respectively [12].

From the calculations of the mean-square displacement it was found [12] that cations are non-diffusive for all temperatures of interest, while for $k_B T/A \geq 1.392$ anions are clearly diffusive; for $k_B T/A = 1.225$ and 1.281 those are slightly diffusive; for $k_B T/A = 1.114$ anions are almost non-diffusive.

The potential energies per ion seem to link in a smooth continuous line, and no significant system-size dependence is obtained. On the other hand, in fluctuations of the potential energies there is observed a rather large system-size dependence for two high temperatures. From the results of the 96-ion system a λ -like anomaly seems to occur around $k_B T/A \approx 1.3$, being similar to the experiment on the specific-heat measurement for CaF_2 [13], while the results of the 324-ion system show a different behavior such that the specific heat increases as the temperature increases [12].

Using the fractional number of anions located in the tetrahedral and interstitial octahedral locations [12], it is found that there is a drop of the fraction of anions in t-sites locations around $k_B T/A \approx 1.3\text{--}1.4$; that is, for the low-temperature side it is nearly one as expected, and for the high-temperature side it decreases to ≈ 0.7 . On the other hand the fraction in the octahedral locations shows a smooth increase as the temperature increases. Around the transition the fraction in the octahedral locations reaches only a few percent, and therefore the transition cannot be described by the usual two-site (tetrahedral and octahedral) model of the order-disorder type. This result is consistent with results of Dickens et al. [14] and Dixon and Gillan [15], but is inconsistent with those of Axe et al. [16].

The x , y , and z coordinates of anions as a function of MC time make clear that anions oscillate with rather large amplitudes, and that they travel between tetrahedral positions in a very short period compared with the residence time of oscillations [12]. The diffusive motion of anions occurs as discrete hops with a large ratio of residence to hopping times. This is consistent

with the molecular dynamics results for CaF_2 [15] and for SrCl_2 [17].

In the Monte Carlo calculation the time-step is not real time. Assuming that the MC time is proportional to the real time, i.e. $t_{\text{MC}} = \tau_s t$, we evaluated the ratio of the diffusion constant to τ_s . We obtained [12] a different temperature dependence for it between the high- and low-temperature regions around $A/k_B T \approx 0.75$, which is similar to common properties observed for the conductivities of superionic conductors of fluorites [18].

Finally we remark that the absolute temperature of the phase transition predicted from $k_B T/A \approx 1.3\text{--}1.4$ with $A = 1.07 \times 10^{-2} e^2/\text{\AA}$ is given by $T_c = 2300\text{--}2500$ K, which is much higher than the experimental value for CaF_2 , $T_c = 1423$ K. However this discrepancy is partly overcome by using a reduced value of A . On the other hand our results show that the temperature range of the superionic phase is predicted to have a value greater than 1.4, which is also larger than that of $\text{CaF}_2 (\approx 1.2)$. Such a large temperature range of the superionic phase suggests that the present model using $n = 12$ will be more suitable to PbF_2 or BaF_2 fluorites rather than CaF_2 , as the former have T_m/T_c or 1.3, respectively. It is of interest to study the n -dependence of our model which will be responsible for specifying these differences among superionic fluorite conductors.

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