Melting properties of sodium halides: molecular dynamics simulation

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Abstract. Molecular dynamics was used to calculate the melting phase transition properties in classical ionic systems. A simplified model of pair potential is considered, with only two terms: the Born-Mayer repulsion and the Coulomb interaction. Preliminary ab initio calculation of the potential parameters was carried out for sodium halides. Regularities in changes of temperature, enthalpy and entropy of melting have been analyzed by direct heating method. It was found that the calculated values of the enthalpy of melting differ from the experimental data less than 5%.

1. Introduction

Alkali halides (AH) is an important class of model objects for which it is possible to perform a molecular dynamics description of a variety of thermodynamic and thermophysical properties, and thus to explain experimental data [1]. Among alkali halides, sodium salts frequently serve as a starting point in the development of methods and approaches, since rock salt is the most common halide in nature. It is not surprising that these objects attract great attention in molecular dynamics studies in spite of the simplicity of pair interactions [2].

The AH melting point is determined by the value of the crystal lattice bonding energy, which is mainly the Coulomb energy in this case. Therefore, the experimentally observed decreasing of melting temperature $T_m$ in the series from sodium fluoride to sodium iodide can be interpreted as follows: the larger the radius of the anion, the lower $T_m$ [3]. It is also well known from the experiment that the entropy of melting $\Delta S_m$ varies slightly in these halides and amounts to about 25 J/(mol K) [4]. It is easy to see that the latent heat of fusion or $\Delta H_m$ (at constant pressure) is in reverse proportion of anionic radius, since $\Delta H_m = T_m \Delta S_m$. In quantitative terms, $\Delta H_m$ drops from 33.35 kJ/mol (NaF) to 23.60 kJ/mol (NaI) [3].

There are two main approaches to the description of melting within the framework of classical molecular dynamics (MD) modeling. The first is to model a separate cluster consisting of several hundred or thousands of particles without imposing periodic boundary conditions. Its advantages include observations of hetero-phase state of matter, if the temperature in the system has reached the melting point [5]. The second consists in the classical simulation of an ensemble with periodic boundary conditions on the initial MD cell, for example, with step-by-step increase in temperature. Here, the thermodynamic properties of the phase are more accurately determined, but there is a problem of overheating [6]. More accurate MD methods for determining the melting point of crystalline ionic compounds with NaCl-type lattice were
proposed by various groups of authors. The paper [7] presents the melting points obtained by the method of calculating the free energy of the solid and liquid phases of NaCl, both consisting of 512 ions. The melting temperature was estimated using the Fumi-Tosi rigid ion model (RIM). Belonoshko [6, 8] used the two-phase simulation method with constant pressure to calculate the melting curve of LiF, NaCl up to pressure of 3 Mbar. The parameters of pair potential were determined from the experiment. It was shown that the agreement between the simulation results and the experimental melting curve is quite satisfactory. Boechle [9,10] calculated melting characteristics (volume change, entropy of melting ) up to 1 Mbar for LiF, NaCl, CsI by means of direct heating of 216 ions at NPT ensemble. Chen [11] simulated melting using the Fumi-Tosi potential in the pressure range 0–30 Mbar for NaCl. For determination of the melting point, the direct heating method was applied to NPT ensemble consisting of 1000 ions. A comparison of the Fumi-Tosi potential RIM model and the shell model [12] for describing the melting of NaCl in the pressure range 0–30 Mbar was carried out in [13] by the single-phase simulation. The calculated melting temperatures for the RIM/Fumi-Tosi model and the shell model overestimate experimental data by 17% and 27%, respectively. The melting curve calculated with Fumi-Tosi model is in good agreement with the results obtained for two-phase simulation.

Detailed results of molecular dynamics simulation of many alkali halides melting are presented in [14]. The authors calculated the melting characteristics of alkali halides using different pair potentials. However, the experimentally observed trends in melting temperature and latent heat in connection with anionic composition of salt in the series of sodium halides have not been analyzed. Note that for NaF, the calculated melting point was two times lower than the experimental value.

In this study, we focus on that part of the pair interaction, which is, in our opinion, determines the trends in the AH melting properties. Namely, for the melting problem, one can neglect the van der Waals interactions in the Born-Huggins-Mayer potential (BHM), focusing instead on the Born-Mayer repulsion, whose parameters can be calculated ab initio. We will show that our approach of simplified potential allows us to obtain reasonable melting properties using a direct heating method, with some systematic overheating are taken into account.

2. Simulation details

An interaction in sodium halides was described by pair approximation. The potential energy function consists of two contributions: the first is the Coulomb term, the second term describes the short-range repulsion of electron shells in exponential form (Born-Mayer):

\[ U_{ij}(r) = \frac{Z_i Z_j e^2}{\varepsilon r} + A_{ij} \exp\left(\frac{-r}{\rho_{ij}}\right), \]

there \(Z_i, Z_j\) are the charges of interacting particles located at a distance \(r\), \(\varepsilon\) is the dielectric constant (equal to 1 in our case), \(e\) is an electron charge. The parameters \(A_{ij}\) and \(\rho_{ij}\) specify the Born-Mayer repulsion.

The parameters of the pair potential for NaX salts (\(X = \text{F, Cl, Br, I}\)) are calculated by fitting the pair potential curve (1) to the functions obtained from ab initio simulation. The second-order Møller-Plesset perturbation theory (MP2) was used [15–17]. Ions were described by means of def2-TZVP split-valence basis sets [18]. The simulated systems were a pair of ions with a total charge of \(2e\), 0 or \(-2e\) for pairs Na–Na, Na–X and X–X, respectively. The energy of such a system was calculated in the range of distances between ions from 1 to 8 Å. At distances from 1 to 4 Å, the calculation was carried out with the step of 0.25 Å; at distances from 4 Å to 8 Å, the step was increased to 1 Å. The calculations were carried out in the ORCA program [19]. For each ion pair, the parameters \(A_{ij}\) and \(\rho_{ij}\) of pair potential (1) were adjusted in order to fit accurately the energy dependence obtained from MP2. Ab initio calculated parameters \(A_{ij}\) and \(\rho_{ij}\) are given in Table 1.
Table 1. Ab initio calculated parameters of pair potential (1) for sodium halides.

| Salts | $A_{ij}$ (eV) | $\rho_{ij}$ (Å) |
|-------|---------------|-----------------|
|       | Na–Na | Na–X | X–X | Na–Na | Na–X | X–X |
| NaF   | 8595   | 2349 | 1062 | 0.175 | 79 | 0.245 | 81 | 0.276 | 45 |
| NaCl  | 2832   | 3318 | 0.281 | 72 | 0.276 | 95 |
| NaBr  | 2338   | 3250 | 0.306 | 95 | 0.330 | 63 |
| NaI   | 1862   | 5667 | 0.340 | 78 | 0.327 | 63 |

Figure 1 illustrates the regular change in the potential energy of sodium-halogen pairs depending on distance. It can be seen that the smaller the halogen anion, the minimum is closer to central ion, with the energy of minimum increases in absolute value.

Simulations of the ionic crystals using pair potential (1) were carried out at external pressure of 1 bar and NPT ensemble containing 512 particles with the step on temperature of 10 K. The time step for the simulations was 5.0 fs; averages were computed over the time 5.0 ns (1 000 000 time steps) simulation. The Coulomb interaction term was evaluated using Ewald summation at a precision of $10^{-5}$. The melting point was determined by the observation of abrupt change of volume of the MD cell. The precision of $T_m$ for the melting point is defined by used increment of $T$. The simulations in this work were performed using the LAMMPS MD software package. The calculations were performed using “Uran” supercomputer of IMM UB RAS.

3. Results and Discussion

The enthalpy of melting was calculated as the difference between the enthalpies of the ensemble in the liquid and solid states at melting temperature. The entropy of melting can be easily found from the thermodynamic relation: $\Delta S_m = \Delta H_m / T_m$.

Table 2 summarizes the results of calculating the temperature, enthalpy and entropy of melting together with the experimental values for sodium halides. The statistical error in
Table 2. Melting properties of sodium halides.

| Salts | \( T_m \) (K) | \( \Delta H_m \) (kJ/mol) | \( \Delta S_m \) (J/(mol K)) |
|-------|---------------|----------------|------------------|
|       | MD exp MD exp | MD exp MD exp | MD exp MD exp |
| NaF   | 1460 1268     | 31.43 33.35    | 21.53 25.71      |
| NaCl  | 1320 1073     | 28.35 28.16    | 21.48 26.08      |
| NaBr  | 1165 1020     | 25.35 26.11    | 21.76 25.62      |
| NaI   | 1065 933      | 23.47 23.60    | 22.04 25.29      |

Figure 2. Calculated temperature dependencies of MD cell volume for sodium halides.

determining the melting temperature is about 1%, enthalpy and entropy of melting – 2%.

Figure 2 shows the heating curves for MD cells for various sodium halides. The experimentally observed regularity of the melting temperature decreasing with the increasing the “size” of the halogen anion can be satisfactorily described by the simplification of pair interaction down to the Born-Mayer repulsion plus the Coulomb term.

4. Conclusion

Our MD calculations based on simplified pair potential with the preliminary ab initio determination of their parameters show satisfactory agreement of the melting point characteristics in general. There is systematic overestimation associated with the chosen method of the MD modeling – direct single-phase heating. It is well known that this approach gives some overheating (about 20% of the \( T_m \) value). However, for sodium halides, such accuracy in describing the trend of the melting temperature with the change of the anion “size” is quite sufficient. For the sodium halides the latent heat of fusion have found to be of quantitative accuracy, and the entropy of melting is somewhat underestimated. Note that the value of the entropy of melting is nearly the constant, which is fully consistent with the experiment.
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References
[1] Lantelme F and Groult H (eds) 2013 Molten salts chemistry: from lab to applications (Burlington, MA: Elsevier)
[2] Sangster M J L and Dixon M 1976 Adv. Phys. 25 247–342
[3] Haynes W M (ed) 2014 CRC Handbook of Chemistry and Physics, 95th Edition (Boca Raton, FL: CRC Press)
[4] Wunderlich B (ed) 2005 Thermal Analysis of Polymeric Materials (Verlag, Berlin, Heidelberg: Springer)
[5] Mei Q S and Lu K 2007 Prog. Mat. Sci. 52 1175–262
[6] Belonoshko A B, Ahuja R and Johansson B 2000 Phys. Rev. B 61 11928–935
[7] Anwar J, Frenkel D and Noro M G 2003 J. Chem. Phys. 118 728–35
[8] Belonoshko A B and Dubrovinsky L S 1996 Am. Mineral. 81 303–16
[9] Boehler R, Ross M and Boercker D B 1996 Phys. Rev. B 53 556–63
[10] Boehler R, Ross M and Boercker D B 1997 Phys. Rev. Lett. 78 4589–92
[11] Chen Q F, Cai L C, Duan S Q and Chen D Q 2004 Chinese Phys. 13 1091–95
[12] Dick B G and Overhauser A W 1958 Phys. Rev. 112 90–103
[13] Sun X W, Chu Y D, Liu Z J, Kong B, Song T and Tian J H 2012 Physica B 407 60–63
[14] Aragones J L, Sanz E, Valerian i C and Vega C 2012 J. Chem. Phys. 137 104507
[15] Møller C and Plesset M S 1934 Phys. Rev. 46 618–22
[16] Pople J A, Seeger R and Krishnan R 1977 Int. J. Quant. Chem. Symp. 11 149–63
[17] Bartlett R J 1981 Ann. Rev. Phys. Chem. 32 359–401
[18] Rappoport D and Furche F 2010 J. Chem. Phys. 133 134105
[19] Neese F 2012 Comp. Mol. Sci. 2 73–78