

## Structural disorder within computer-simulated crystalline clusters of alkali halides

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The method of molecular-dynamics (MD) simulation of alkali halides and computer code CLUSTER were developed. The method was applied to calculate structural and kinetic characteristics of small clusters of RbBr, NaBr, NaI, NaCl, KI, and KCl from 10 K to their assumed melting points ( $T_m$ ). The temperature dependence of relative mean square vibrational amplitudes has a universal character and satisfies the Lindemann criterion of melting in the vicinity of  $T_m$ . In spite of the size effect the values of  $T_m$  for all the salts except NaI agree within the error bars of about 100 K with the bulk melting temperatures. The anomalous behavior of NaI at about 200 K below its experimental melting point is interpreted in terms of enhanced mobility of  $\text{Na}^+$  ions linked to the anomalous enhancement of conductivity observed previously for this salt.

Computer simulation of alkali halides predicts rather successfully their bulk structural<sup>1</sup> and thermodynamic<sup>2</sup> properties. However, as one can see from below, the detailed picture of ionic behavior within a small cluster of a few interionic distances still may contribute a lot to our understanding of mechanisms of their conduction and melting.

We performed a series of molecular-dynamics (MD) calculations for clusters of 125 ( $5 \times 5 \times 5$ ) and 216 ( $6 \times 6 \times 6$ ) ions of NaCl, NaBr, NaI, KCl, KI, and RbBr and then traced the detailed behavior of only inner 27 ( $3 \times 3 \times 3$ ) and consequently 8 ( $2 \times 2 \times 2$ ) core ions less influenced by surface effects.

The interionic potentials we used were the superposition of Coulomb and Born-Mayer terms:

$$V_{ij} = \frac{Z_i Z_j}{r_{ij}} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho}\right), \quad (1)$$

where  $Z_i$  and  $Z_j$  are the charges of ions  $i$  and  $j$ , respectively, separated by a distance  $r_{ij}$ , and  $A_{ij}$  and  $\rho$  are the repulsion parameters taken from crystal data.<sup>3,4</sup> The temperature is defined as the mean kinetic energy per particle.

To perform a MD simulation of a cluster one should first prepare a proper sample close to a really expected equilibrated structure (see, e.g., Ref. 5). We used an algorithm of a "staircaselike equilibration" based on rescaling of the ions velocities in order to remove an excess of total energy caused by an arbitrary choice of the initial low-temperature ions configuration. The energy conservation was being kept better than 1 part of  $10^4$  over a run of 0.1 nsec. Then we enhanced the temperature (ions velocities) of this sample using a stepwise heating process.<sup>6,7</sup>

The results of such a procedure for average configurations of NaCl are shown in Figs. 1(a) and 1(b), corresponding to temperatures 100 K and 950 K, respectively.

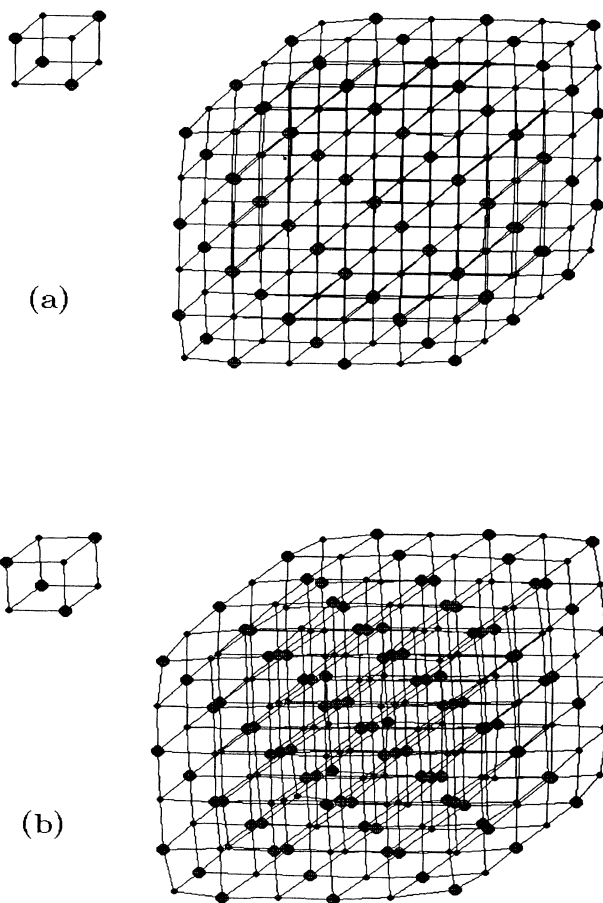


FIG. 1.  $6 \times 6 \times 6$  NaCl cluster at 100 K (a) and 950 K (b); shown also is the  $2 \times 2 \times 2$  inner core of NaCl cluster at 100 K (a) and 950 K (b).

TABLE I. Comparison of bond lengths as obtained from MD simulations at 300 K, 400 K, and 500 K (left column) with crystallographic data (Ref. 8) (right column), Lindemann criterion of melting as obtained in simulations (left column), and in Ref. 10 (right column).

Salt	300 K		400 K		500 K		$X_m^2 \times 10^{-2}$	
	$d_{\text{sim}}$ (Å)	$d_{\text{expt}}$ (Å)	$d_{\text{sim}}$ (Å)	$d_{\text{expt}}$ (Å)	$d_{\text{sim}}$ (Å)	$d_{\text{expt}}$ (Å)	This work	Ref. 10
NaI	3.25	3.24	3.26	3.25	3.28	3.27	1.1	1.3
NaCl	2.83	2.82	2.84	2.83	2.85	2.84	1.0	1.3
NaBr	3.02	2.99	3.03	3.00	3.04	3.01	1.0	1.4
KCl	3.20	3.15	3.22	3.16	3.24	3.17	1.2	1.1
KI	3.61	3.53	3.62	3.55	3.64	3.56	1.2	1.5
RbBr	3.49	3.45	3.51	3.46	3.53	3.48	1.0	1.1

While the average parameters of such deformed cubes might be rather different from the bulk equilibrated crystal parameters, its inner parts [Figs. 1(a) and 1(b), insets] still keep relatively high cubic order.

Table I gives the values of bond lengths  $d$  of the inner cores (27 or 8) of the simulated clusters in comparison with the experimental data for corresponding bulk crystalline salts.<sup>8</sup> As one can see they agree rather well (better than 2.5%).

The anharmonicity of atomic vibrations and vacancies creation become significant only at high temperature. Thus in the classical limit  $T \ll T_m$  we expect the harmonic approximation to be valid. This must lead to the universal classical equation

$$\langle E \rangle = 3Nk_B T, \quad (2)$$

where  $\langle E \rangle$  is the total energy,  $N$  the number of atoms, and  $k_B$  the Boltzmann constant. Figure 2 demonstrates the validity of the Eq. (2) for the caloric curves of all the investigated salts up to rather high temperature. Caloric curves of real crystals would deviate from our curves below Debye temperature due to the quantum character of atomic motion which cannot be properly accounted for within our classical approximation. This, however, does not affect our results at higher temperatures.

Figure 3 presents the mean-square relative fluctuations

of ions  $(\Delta x/a)^2$ , where  $\Delta x$  is the vibrational amplitude,  $a = 2d$  is the lattice constant, within the cores of clusters as a function of temperature. The first thing to be seen in the picture is a universality of the curve for all the salts but NaI. This result basically agrees with the universality obtained in calculations of Debye-Waller factors.<sup>9</sup> It demonstrates both a validity of a quasiharmonic vibrations theory for Debye-Waller factor of salts at the interval up to 500–600 K (about  $2/3 T_m$ ) and a universal character of deviation from harmonicity for higher temperature. The values of mean-square fluctuations at the higher ends of a stability range for all the salts are close to the expected Lindemann criterion value<sup>10</sup>  $X_m^2 = (\Delta x/a)^2$  at  $T \approx T_m$  (Table I). The corresponding temperatures (except NaI)  $T_m$  agree within their error bars with the melting temperatures of the bulk crystalline salts.

Figure 4 presents the same kind of data for NaCl clusters of 125 and 216 particles (and consequently averaged within the inner core of 27 and 8 ions). Since one can not see a noticeable difference between the final data, it seems rather reasonable at the present accuracy of simulation to neglect the possible influence of a cluster size and charge. It is amazing that a 27-ion core separated only by 1 layer from the surface of a charged 125-ion cluster behaves almost the same way as an 8-ion core of a neutral 216-ion cluster separated from the surface by even two layers.

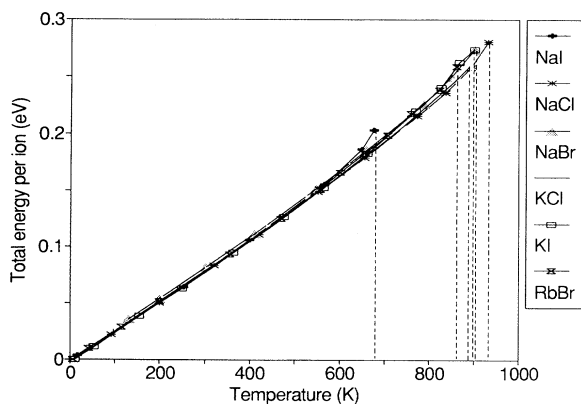


FIG. 2. Caloric curves. The dashed lines indicate the ends of the stability ranges of the clusters.

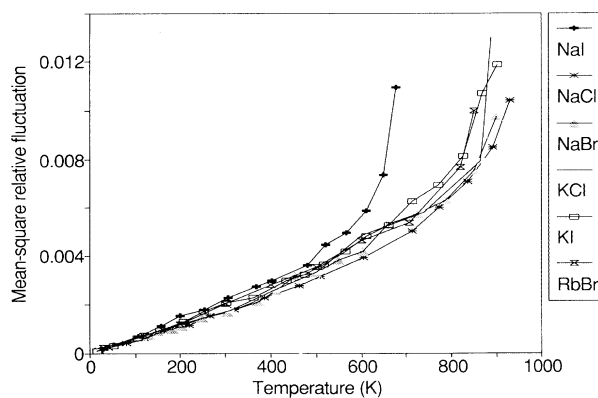


FIG. 3. Mean-square relative fluctuations of the 27 inner core ions within the  $5 \times 5 \times 5$  cluster.

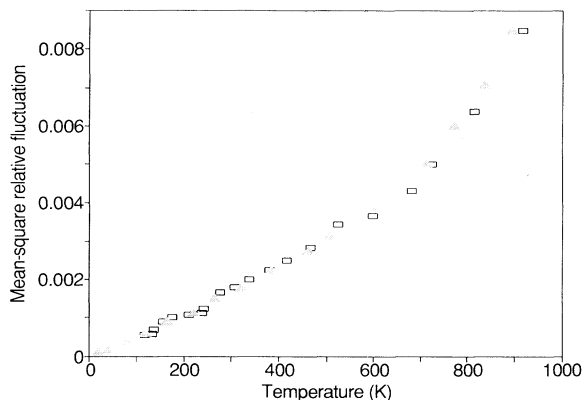


FIG. 4. Mean-square relative fluctuations of the 27 and 8 inner core ions within the  $5 \times 5 \times 5$  (triangles) and  $6 \times 6 \times 6$  (squares) NaCl clusters, respectively.

The calculated  $T_m$  of NaI is dramatically lower (700 K) than the experimental figure (930 K). This makes us try to probe deeper. Comparing the two ionic size ratios  $R_I/R_{Na} = 2.2$  and  $R_{Cl}/R_{Na} = 1.8$  one can expect a higher mobility of  $Na^+$  in NaI. Therefore let us trace a time dependence of a central  $Na^+$  ion position (radius

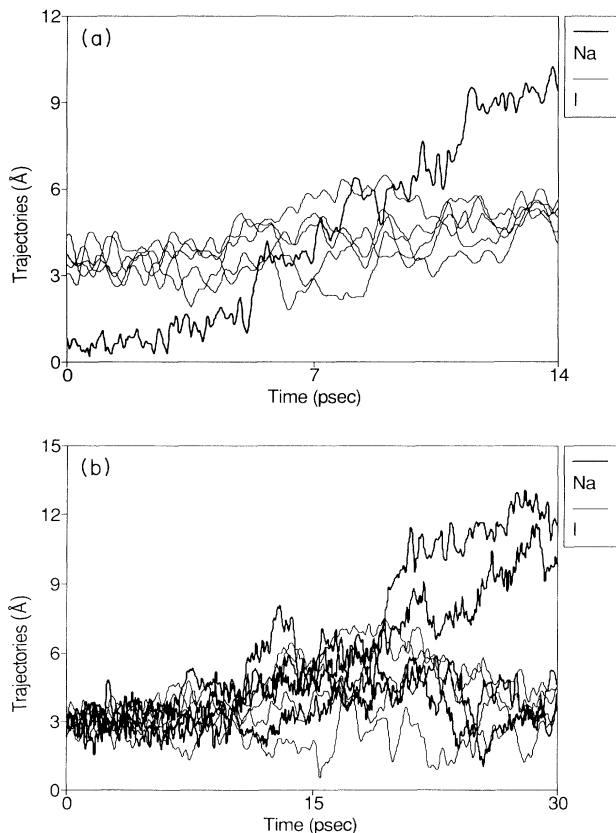


FIG. 5. Relative positions of sodium and iodine ions from the center of the  $5 \times 5 \times 5$  (a) and  $6 \times 6 \times 6$  (b) clusters vs simulation time at  $T \approx 700$  K.

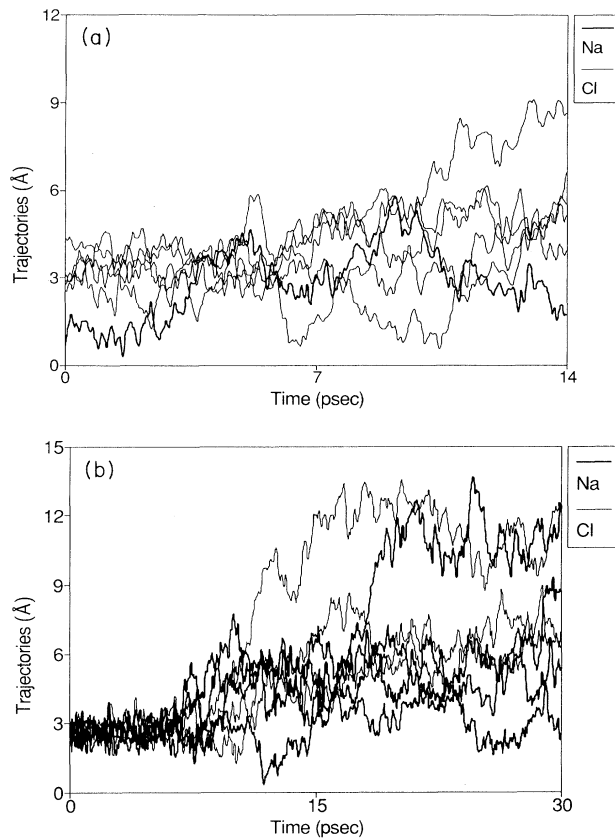


FIG. 6. Relative positions of sodium and chlorine ions from the center of the  $5 \times 5 \times 5$  (a) and  $6 \times 6 \times 6$  (b) clusters vs simulation time at  $T \approx 950$  K.

vector) within the inner core of the 125-ion cluster of NaI. As one can see from Fig. 5(a) its trajectory at high temperature drives it rather quickly to the surface, while the anions remain basically at their sites. Thus it should lead to a high conduction in this salt at elevated temperature still below the melting. This trend is confirmed for a cluster of 216 ions as well [Fig. 5(b)]. Cations again diffuse through the cluster almost freely spending at their crystalline sites not more than  $2 \times 10^{-12}$  sec. In accordance with our expectation just the opposite is true for corresponding cations within a NaCl cluster [Figs. 6(a) and 6(b)]. The sodium ions remain within the core until the melting occurs. Thus the conduction of the NaCl cluster preserves its small value up to its melting point.

It might happen (if it is confirmed) that a  $T_m$  point calculated in a case of NaI simulations has only little to do with its melting but is actually associated with another additional transition in this salt similar to superionicity in analogy with Ref. 11. This interpretation would agree with our experimental observation<sup>12</sup> of the enhanced conductivity well below the melting point of this salt.

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