Range effects of the Coulombic forces on structures, thermodynamic properties and potential energy landscapes: (KCl)$_{32}$ and related systems

Chengjui Wang$^{a,b}$, R. Stephen Berry$^a$, Julius Jellinek$^{b,*}$

$^a$Department of Chemistry and The James Franck Institute, The University of Chicago, Chicago, IL 60637, United States
$^b$Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, United States

1. Introduction

Since Goldstein recognized the key role of potential energy surfaces (PES) in determining the structures, dynamics and thermodynamics of glasses [1], the goal of understanding and explaining properties of systems in terms of topographies of their potential energy surfaces has become a major pursuit in physics, chemistry, and biology [2–7]. Achieving this goal has been greatly aided by advances in computer technologies and computational methodologies. Indeed, it became possible to search for and find stationary points (minima and saddles) of potential energy surfaces of systems of ever larger sizes and increasing degree of complexity, and to analyze the structural characteristics and dynamical/thermodynamical behavior of these systems in terms of features of their potential energy landscapes [2,3,8–19].

A parameter that plays a central role in determining the details of a potential energy landscape is the range of interatomic interaction(s) [we limit our consideration here to the case of pairwise-additive potentials]. Indeed, it has been shown that the potential energy surface of a homogeneous cluster bounded by a long-range interatomic interaction is smoother and simpler than that of a cluster bounded by a short-range interaction; it has also been shown that shortening of the range of interaction facilitates the size-induced transition in the structure of the energetically most preferred form of a cluster from icosahedral to face-centered-cubic [8–11]. Yet another qualitative finding is that systems with long-range interactions tend to be structure-seekers, whereas those with short-range interactions are glass-formers [12–14].

The multiplicity of effects of the range of interatomic interactions, as they exhibit themselves in homogeneous systems, has been explored and characterized quite extensively, at least for systems with pairwise-additive potentials (cf., e.g., [8–11]; and references therein). In contrast, the subject has been addressed only in a limited way for heterogeneous, in particular ionically bonded, systems [12–14]. The goal of this study is to explore and to characterize in greater detail the role and the consequences of the extents of the interaction ranges in binary ionically bonded clusters. We choose as a paradigmatic case a 64-atom binary cluster that represents (KCl)$_{32}$ and its derivative analogs. The interaction between the atoms, more precisely ions, is mimicked by a Coulomb term with a variable degree of shielding combined with a Born–Mayer term to represent core repulsion. The study explores and characterizes the structural and dynamical consequences of varying the shielding in the Coulomb part. These consequences include departure from the rocksalt structure, which is the native one for (KCl)$_{32}$, to other energetically more preferred structures, and a gradual disappearance of the portion with a negative value in the

© 2011 Elsevier B.V. All rights reserved.
energy-dependence of the heat capacity, both caused by shortening of the range of the Coulomb interactions. The changes in the dynamical properties are correlated with and explained in terms of the changes in the spectra of the stationary points (minima and saddles) of the potential energy surface caused by the changes in the shielding of the Coulomb part.

The rest of the paper is organized as follows. The methodological and computational details are outlined in Section 2. The results and their discussion are presented in Section 3. The concluding remarks are summarized in Section 4.

2. Methodological and computational details

The primitive system of the current study is (KCl)$_{32}$, which is modeled by the Coulomb interaction plus the Born–Mayer potential [20,21], i.e., the pair potential between any two ions $i$ and $j$ with charges $q_i$ and $q_j$, respectively, separated by the distance $r_{ij}$ is given as

$$V_{ij} = \frac{q_i q_j}{r_{ij}} + A_{ij} e^{-r_{ij}/\rho}.$$  

This model was originally developed for alkali halide systems, in which all atomic components are treated as spherical ions with exponential repulsive cores; for the KCl system, the parameters of the Born–Mayer term, as defined by Tosi and Fumi [20], are $A_{++} = 1555.21$ eV, $A_{+-} = 1786.91$ eV, $A_{-+} = 1924.80$ eV and $\rho = 0.337 \text{Å}$, where “+” stands for K and “−” stands for Cl. The charges on the ions are treated as fixed point charges, and the polarization effects are neglected. Earlier studies have shown that inclusion of polarization causes only minor changes in the equilibrium structural forms as compared to the changes caused by varying the parameters of the Born–Mayer term [21–24].

Our approach is to introduce parameters $\gamma_i$, $\gamma_j$ and $B$, which we will refer to as shielding parameters, into the Coulomb-like part of the total energy as follows

$$\Phi = \sum_i \sum_j U_{ij} = \sum_i \sum_j \left[ B \frac{q_i q_j}{r_{ij}} e^{-(r_{ij}/\rho) \gamma_i \gamma_j} + A_{ij} e^{-(r_{ij}/\rho)} \right].$$

Parameters $\gamma_i$ and $\gamma_j$ allow one to change the range of the Coulomb interaction between ions $i$ and $j$, and parameter $B$ allows for scaling its magnitude. When $\gamma_i = \gamma_j = 0$ and $B = 1$ one recovers the unshielded pair interaction defined by Eq. (1). In what follows, we restrict our consideration to the case $\gamma_i = \gamma_j = \gamma$, so that all the pair Coulomb-like interactions are characterized by the same “shielding length” $s = 1/\gamma$. Furthermore, since our goal is to explore the effects of the range of the Coulomb interaction (as controlled by the value of $\gamma$) alone, i.e., without the intervening effects of the changes in the depth of the cation–anion pair potential that accompany the changes in the value of $\gamma$, for each chosen $\gamma$ we selected that single parameter space ($\gamma$, $B$) as a function of energy is analyzed in terms of three characteristic quantities (see below), which are generated employing constant-energy molecular dynamics simulations. The trajectories are propagated using the Verlet algorithm [25] with a time step of 3 fs, which assures conservation of the total energy within 0.01% even in the longest runs. The initial momenta of the atoms are zero. This assures that the systems’ translational and rotational energies are and remain zero. At each fixed energy outside the solid-to-liquid-like transition range, the trajectories are propagated for $10^6$ time steps. At energies within this range the length of the trajectories is $10^7$.

we omit indication of the units of $\gamma_i$. It is clear from the figure that the shapes of the cation–cation and anion–anion pair potentials corresponding to the same value of $\gamma$ are essentially the same. The reason for this is that, except for the shortest distances, these potentials are dominated by the Coulomb interaction. The top panel of the figure illustrates the extent of the changes in the range of the cation–anion pair potential as $\gamma$ increases from 0 to 0.5.

The dynamical/thermodynamical behavior of the systems (each corresponds to a different fixed values of the shielding parameter $\gamma$) as a function of energy is analyzed in terms of three characteristic quantities (see below), which are generated employing constant-energy molecular dynamics simulations. The trajectories are propagated using the Verlet algorithm [25] with a time step of 3 fs, which assures conservation of the total energy within 0.01% even in the longest runs. The initial momenta of the systems are chosen to represent some nonequilibrium low-energy configurations. The initial momenta of the atoms are zero. This assures that the systems’ translational and rotational energies are and remain zero. At each fixed energy outside the solid-to-liquid-like transition range, the trajectories are propagated for $10^6$ time steps. At energies within this range the length of the trajectories is $10^7$.

Table 1

<table>
<thead>
<tr>
<th>$\gamma$ (Å$^{-1}$)</th>
<th>0.000</th>
<th>0.125</th>
<th>0.250</th>
<th>0.350</th>
<th>0.400</th>
<th>0.450</th>
<th>0.500</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B$</td>
<td>1.000</td>
<td>1.879</td>
<td>3.368</td>
<td>5.230</td>
<td>6.464</td>
<td>7.948</td>
<td>9.723</td>
</tr>
<tr>
<td>$s$ (Å)</td>
<td>$\infty$</td>
<td>8.000</td>
<td>4.000</td>
<td>2.857</td>
<td>2.500</td>
<td>2.222</td>
<td>2.000</td>
</tr>
</tbody>
</table>

Fig. 1. The shielded Coulomb plus Born–Mayer potential for the indicated values of the shielding parameters $\gamma$ (Å$^{-1}$) and $B$ (unitless). Upper panel: $U_-$, the cation–anion pair potential part; middle panel: $U_{++}$, the cation–cation pair potential part; lower panel: $U_+$, the anion–anion pair potential part.
steps. The increase in the (vibrational) energy of the systems from one trajectory to the other is achieved through uniform scaling of the momenta of the atoms. The characteristic quantities computed along the trajectories include the following:

1. Caloric curve, i.e., the microcanonical dynamical (vibrational) temperature [26,27]

\[
T = \frac{1}{k_B} \left( \frac{3N-6}{2} - 1 \right) \left( E_{\text{Kin}}^{-1} \right)^{-1},
\]

as a function of the system energy. In this equation, \( N \) is the number of atoms in the system, \( k_B \) is the Boltzmann constant, \( E_{\text{Kin}}^{-1} \) is the inverse of the system kinetic energy, and \( \langle \cdot \rangle \) stands for the time average over the entire trajectory.

2. Relative root-mean-square fluctuation in the interatomic distances [28]

\[
\delta = \frac{2}{N(N-1)} \sum_{j>i} \left( \langle r_{ij}^2 \rangle - \langle r_{ij} \rangle^2 \right)^{1/2},
\]

which is an analog of the Lindemann criterion for crystals [29].

3. Heat capacity (per ion) in units of \( k_B \) [26–28,30,31]

\[
C = \frac{2}{N(N-1)} \left[ \left( \frac{3N-6}{2} - 1 \right) - N \left( \frac{3N-6}{2} - 2 \right) \langle E_{\text{Kin}}^{-1} \rangle \right]^{-1},
\]

where \( E_{\text{Kin}}^{-2} \) is the inverse of the square of the system’s kinetic energy.

The topographies of the potential energy surfaces corresponding to different values of the shielding parameter \( \gamma \) are characterized through the distributions of their minima and saddle points (transition states). For each surface, the minima are obtained by applying gradient-based techniques [32] to a large number of configurations generated along a long high-energy trajectory that corresponds to a melted state of the system (runs of \( 10^7 \) time steps were used and the configuration were sampled every 200 steps, i.e., with a time interval of about a vibrational period\(^1\)). Each local minimum found was used as a starting point of a search for a transition state using the softest mode following methodology\(^2\) as implemented in the OPTIM package [34]. The same package was then employed to find the minimum on the “other side” of the transition state.

3. Results and discussion

Figs. 2–8 show three characteristic quantities – the caloric curve, the heat capacity, and the rms fluctuation in the interatomic distances, all considered as a function of energy – for the 64-atom bin-

\(^1\) The typical vibrational period of potassium chloride systems is estimated to be about 0.5 ps [33].

\(^2\) A question can be asked about the possible effect on the resulting distributions of the stationary points, in particular transition states, of a potential energy surface of the fact that the search is limited to the “direction” of the lowest frequency mode only. To address this question we performed select parallel searches that used all the 2(3N-6) directions defined by the 3N-6 normal modes of the system. Based on the comparison of about 50,000 minimum-saddle-minimum triplets obtained in these two ways, we have concluded that the effect is only minor and can be neglected.
A global rapid increase in $\Delta(E)$, the rms fluctuation in the interatomic distances, as a function of total energy $E$ indicates a transition that is generally called solid-like to liquid-like phase change [37]. (The expression “phase transition” has been deliberately avoided because this term usually implies phenomena in bulk systems, e.g., a discontinuous first-order melting transition.) In our case, the finite energy range of the phase change as exhibited by $\Delta(E)$ is coincident with those in $T(E)$ and $C(E)$, although the onset of the change in $T(E)$ is relatively subtle. The structural changes are illustrated in the graph by some representative conformations visited at several selected energies along the thermal history. With these conformations in hand, we learn how the cluster samples its various structural forms with the increasing energy. Starting from the lowest energy conformation – the cubic rocksalt structure, the cluster vibrates only around its most stable isomer until the energy becomes higher than $-3.18$ eV/ion, the onset energy towards eventual full melting. When the system energy is higher than $-3.18$ eV/ion but lower than $-3.08$ eV/ion, the cubic form undergoes substantial distortions and starts to rearrange into other higher energy isomers, which have been called nonwetted structures [18]; in these, the cluster is partly regular, rocksalt-like, and partly highly disordered, with the disordered part on one side and the ordered on the other. When the system energy becomes higher than $-3.08$ eV/ion, the dominant conformations sampled by the trajectories are the completely disordered (amorphous) structures. The inclusion of these in the sampling is responsible for another change in the $\Delta(E)$ curve, which is represented by a shoulder that connects the rapidly changing part of the curve with its slowly varying part at higher energies. We will call this behavior two-stage melting.

The first stage corresponds to the transition from the cubic rocksalt structure to the nonwetted ones, while the second stage represents the transition from the nonwetted structures to the completely disordered ones. The trajectories have to be long enough to assure a statistically correct sampling of the different structures accessible at each energy. This is particularly true for energies representing the transition region from the solid-like to the liquid-like form. Figs. 3 and 4 display the results for shielding parameters $\gamma = 0.125$ and $\gamma = 0.250$, respectively. One immediately recognizes the two peculiarities – the negative heat capacity and the two-stage melting – characteristic of the $\gamma = 0$ case. Although qualitatively the transition from the solid-like to the liquid-like form is similar to that of the $\gamma = 0$ case, quantitatively it undergoes significant successive shifts to lower energies as $\gamma$ increases, and there is also a slight increase in the width of the energy region over which the transition takes place. We return to the discussion of these points below.

Fig. 5 shows the results for the shielding parameter $\gamma = 0.350$. One notices a further shift of the transition region to lower energies and a further slight increase in its width. However, the indication for a two-stage melting (shoulder in the $\Delta(E)$ curve) largely disappears, and the energy range over which the heat capacity is negative becomes narrow. In fact, the negative-valued portion of the heat capacity shown as a dashed line is a schematic representation, rather than a result of calculations, of what one expects based on the presence of a loop in the caloric curve. The energy grid used (0.01 eV/ion) does not allow for a numerical realization of the negative-valued segment of the heat capacity as a continuous curve.

Fig. 3. The same as Fig. 2, but for $\gamma = 0.125$, $B = 1.879$.

Fig. 4. The same as Fig. 2, but for $\gamma = 0.250$, $B = 3.368$. 

Fig. 5.
The case of \( c = 0.400 \) is quite intricate as indicated by the graphs of Fig. 6. The major difference from the earlier cases is a substantial broadening of the transition region, rather than its shift. As in the case of \( c = 0.350 \), we indicate schematically the narrow negative-valued portion of \( C(T) \) by a dashed line (the first apparent peak in the \( C(T) \) graph is a two-point discontinuity rather than a true peak). The \( \delta(E) \) graph suggests restoration of a two-stage type transition. The nature of the stages, however, is somewhat different from those described above. Whereas the first stage still corresponds to transition from sampling only the catchment area of the cubic structure to sampling those parts of the configuration space that also include the so-called nonwetted structures[18], the second stage represents inclusion in the sampling of hollow cage conformations. Inspection of the structures sampled by the trajectory via computer generated movies indicates that these cage conformations are quite “rigid” in that the motions of the atoms in them are quite confined. Further increase of the energy eventually leads yet to another transition signified by an energetically well separated peak – this time a real one – in the heat capacity graph. This peak represents the beginning of inclusion in the sampling of space-filling amorphous structures and eventual melting of the system. Trajectories as long as \( 10^8 \) time steps (300 ns) were run in this case.

As found in our global minimum searches[38], a hollow cage structure becomes the lowest energy conformation of the cluster when \( \gamma = 0.450 \) (Fig. 7) and \( \gamma = 0.500 \) (Fig. 8). As the energy of the system is increased, it escapes from its most stable cage form and starts to visit higher energy conformations. The analysis indicates that the higher energy structures that are visited first are still hollow cages, but the shapes of these cages are different from that of the lowest-energy one. The inclusion in the sampling of new hollow cage forms reveals itself as stepwise sharp changes in the calculated \( \delta(E) \) curve, but the corresponding changes in the \( T(E) \) and \( C(E) \) graphs remain smooth. This implies that the energy of each next accessible cage is not very different from that of the one that preceded it. As the energy continues to increase, the graphs of \( C(T) \) develop a small maximum. Inspection of the trajectories at these elevated energies shows that it is still the cage structures that dominate the configuration space sampled. Only at energies that are higher than that corresponding to the maximum in the \( C(T) \) graph does a different type of structures (the space-filling amorphous) become accessible to the MD trajectories.

The above results lead to the following cumulative picture of the dynamical effects of the range of the Coulombic force. As the value of the shielding parameter \( \gamma \) increases and, consequently, the range of the Coulombic force decreases, the negative-valued segment in the graph of the heat capacity becomes less pronounced and eventually disappears. In order to understand this behavior, we plotted the distributions of the energies for both the minima and the saddles of the PES for various values of \( \gamma \) as shown in Fig. 9. For the unshielded case (\( \gamma = 0 \), panel (a)), the distributions are sharply peaked, which indicates that a large “area” of the configuration space associated with higher energy structures becomes abruptly accessible for sampling as the energy of the system is increased. As the value of \( \gamma \) grows from 0 to 0.125, 0.250 and 0.350 (panels (b–d)), the distributions undergo significant successive shifts to lower energies accompanied by a slight broadening, but over all they remain relatively narrow. Consequently, the man-
ner in which a manifold of higher energy structures gets involved in the sampling with the increase of energy is similar to that of the \( \gamma = 0 \) case, i.e., abrupt, although with some degree of attenuation. At \( \gamma = 0.400 \) (panel (e)), the shift of the distributions is only moderate, as gauged by their high-energy ends, and the dominant change is their broadening in the direction of low energies. At \( \gamma = 0.450 \) and 0.500 (panels (f) and (g)), the distributions do not shift any more, but their broadening in the direction of low energies becomes larger, which means that the number of the minima (and the saddles) of the system increases and their energies become more evenly distributed. As a consequence, the higher energy structures get involved in the sampling in a gradual way as the energy of the system is increased.

The noted features in the distributions of the minima and the saddles and the changes in these features with the increase of \( \gamma \) explain the reason for the existence and gradual elimination of the negative-valued segments in the \( C(T) \) graphs. An abrupt inclusion in sampling of large portions of configuration space with high potential energy by a trajectory of constant total energy translates into a decrease of the overall temperature of the system, or, alternatively, negative heat capacity. As the inclusion of the higher energy parts of the configuration space in the sampling becomes more gradual, the negative-valued portions in \( C(T) \) become smaller and eventually disappear. An interesting observation is that the distributions of the saddles largely mimic the distributions of the minima for all values of \( \gamma \) with a minor shift that increases somewhat for larger values of \( \gamma \) (panel (h) of Fig. 9 – the circles). One also notes the nonmonotonic trend in the energy gap between the two lowest energy structures of the cluster as a function of \( \gamma \) (panel (h) of Fig. 9 – the crosses). First this gap increases as \( \gamma \) changes from 0 to 0.3 and then decreases.

As indicated above, the range of the Coulombic interaction affects the structure of the energetically most preferred conformation of the system. It is of interest to examine the variations in the energies of the different structures as a function of the shielding parameter \( \gamma \). Fig. 10 shows these variations for the rocksalt structure, which is found to be the most preferred for values of \( \gamma = 0, 0.125, 0.250, 0.350 \) and 0.400, and a hollow cage conformation that is the most stable for \( \gamma = 0.450 \) and 0.500. The energies of both structures decrease as the range of the Coulombic force decreases, and at the value of \( \gamma \) of about 0.43 the two switch order. The decrease in the energies of the different structures (as well as of the barriers that separate them) and the switches in their ordering triggered by an increase of \( \gamma \) are reflected in the described above \( \gamma \)-dependent changes in the energy distribution functions of the minima (and the saddles) and the \( \gamma \)-specific patterns of dynamical/thermal behavior as a function of energy.

Our findings on the effects of the range of the Coulombic interaction are consistent with the results of earlier studies on the role of the interaction range. It has been shown that potential energy surfaces of systems interacting via the Morse potential exhibit many saddles when the interaction range is short, and none when the interaction range is sufficiently long [8]. In a study that explored the effect of changing the formal charges of species from ++1 to ++2 in ionic systems such, e.g., as MgO clusters, it has been found that lower charges favor compact rocksalt-like structures, whereas higher formal charges prefer hollow cages [39].

Finally, we remark on the \( \gamma \)-dependence of the “melting temperature”. Even though the hallmark of finite systems is that the
melting-like transition in them takes place over a finite range of energies (or temperatures), one can define a “melting temperature” using the following recipes. The first is based on the energy dependence of the caloric curve and/or the heat capacity. When there is a loop in the caloric curve, the melting temperature is defined as the average of the two temperatures corresponding to the turning points of the loop. When the caloric curve does not exhibit a loop, the melting temperature is defined by the energy at which the heat capacity attains its maximum. The second recipe is based on the energy-dependence of the rms fluctuation in the interatomic distances. The melting temperature is defined by the energy at which \( \langle E \rangle \) becomes essentially flat, or very slowly varying, after an abrupt increase; admittedly, this second definition is somewhat less unambiguous. The results are shown in Fig. 11. The two recipes produce similar melting temperatures for some values of \( c \), especially those that are smaller, and different ones for others. Both, however, agree in that the melting temperature changes nonmonotonically with \( c \). The reason for this is the complexity of the \( c \)-dependent variations in the topography of the potential energy surface, elements of which are presented and discussed above. One can notice, for example, a correlation between the behavior of the melting temperature(s), Fig. 11, and that of the gap in the energies of the two most stable structures of the cluster, panel (h) of Fig. 9, over \( \gamma \) values from 0 to 0.375, where the rocksalt structure is the lowest energy form of the cluster and the saddles with \( \gamma \) is a substantial shift to lower energies, and the graphs of the caloric curve exhibit well developed loops that give rise to negative heat capacity.

4. Concluding remarks

In this paper we addressed the subject of structural and dynamical/thermal effects of the range of the Coulombic interaction in fi-
nite-sized systems. As a paradigmatic case, we considered a 64-atom binary cluster that represents (KCl)$_{32}$ and its derivative analogs. The interatomic interactions in (KCl)$_{32}$ are described by a Coulomb plus Born–Mayer potential. The potentials of the derivative systems are generated by introducing a shielding parameter into the Coulombic part of the interactions; more precisely, two (dependent) parameters are used to keep the well depth of the attractive pair interactions constant. This study complements earlier explorations of the effects of the range of interatomic interactions in homogeneous finite-size systems.

The most stable conformation of (KCl)$_{32}$ has rocksalt structure. The most stable conformations of its derivative analogs are also of rocksalt type, provided the value of the shielding parameter $\gamma$ is small or moderate. Further increase in the degree of shielding or, alternatively, reduction in the range of the Coulombic forces leads to a switch from the rocksalt to hollow cage type structures as the energetically most favored ones.

Shielding of the Coulombic part of the potential leads not only to quantitative, but also qualitative changes in the dynamical/thermal properties of the 64-atom cluster, in particular its transition from solid-like to liquid-like form. The most prominent qualitative change is that the pattern of transition with a loop in the caloric curve and discontinuities coupled with a negative-valued segment in the heat capacity, which is characteristic of long-range Coulombic interactions, transforms into a pattern of transition with only smooth and monotonic variations in both the caloric curve and the heat capacity – the latter displays a smooth moderate maximum – for short-range Coulombic forces. This transformation is “mediated” by a more complex pattern, characteristic of mid-range Coulombic forces, which exhibits a small loop in the heat capacity accompanied by discontinuities and a narrow negative-valued segment in the heat capacity, which also contains an energetically separated smooth moderate maximum.

The cause of the changes in both the structural and the dynamical/thermal properties of the cluster with the range of the Coulombic interaction is the change in the topography of the underlying potential energy surface. The latter is characterized for different values of the shielding parameter in terms of quantities such as energy distribution functions of its minima and saddles, gap between the energies of its two deepest minima, and others. It is ultimately the shielding-dependent changes in these quantities that correlate with and explain the complex transformations in the nature and energy ordering of the different structural forms and in the patterns of the dynamical/thermal behavior of finite ionically bonded systems with the change of the range of the Coulombic interaction.

Acknowledgements

This work was performed as part of the activities of the Joint Theory Institute of the University of Chicago and Argonne National Laboratory. J.J. was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences and Biosciences, US Department of Energy under Contract No. DE-AC02-06CH11357. C.W. would like to thank Dr. Jason R. Green for helpful discussions. R.S.B. would like to acknowledge the hospitality of the Aspen Center for Physics, where some of his work was carried out.

References


[38] C. Wang et al., in preparation.