

Phase Changes, Nonwetting and Coexistence: (KCl)₃₂

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Abstract. Binary clusters of ionic substances exhibit several properties that make them quite different from homogeneous clusters representable by pairwise Lennard-Jones or Morse potentials. While the potential energy surfaces of clusters of only a few or several pairs of ions can be explored in microscopic detail, clusters of the size of (KCl)₃₂ must be examined statistically. The stable structures of (KCl)₃₂ can be put into four useful categories: (1) the rocksalt-like ground state (2) slightly defective crystal-like structures (3) “non-wetting” structures that are partly rocksalt-like and partly amorphous and (4) the amorphous structures. A method is presented to estimate the density of configurational states as a function of energy and, from it, the partition function and thermodynamic properties of (KCl)₃₂. Solid and liquid forms of this cluster can coexist in measurable quantities over a significant range of temperatures. However, the times required for the cluster to show ergodic exploration of solid-like and liquid-like regions of phase space is beyond the limits of conventional dynamic simulations.

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1. Introduction

The phase behavior of Lennard-Jones clusters, i.e., rare gas systems, has been extensively studied and consequently is now well-understood. To understand more thoroughly the general phase behavior of clusters, other cluster systems must be examined and compared with the rare gas clusters. Binary clusters of ionic substances are interesting clusters to study because they exhibit properties that make them very different from the rare gas clusters and also because it is anticipated that, unlike the rare gas clusters, the phase behavior of pure ionic clusters might be experimentally approachable.

Previously [1] we reported on the phase behavior of small KCl clusters, namely, (KCl)₄ and (KCl)₅. In that

study the underlying potential energy surface of the cluster was mapped out in exhaustive detail. The dynamics and thermodynamics of the cluster, as revealed by molecular dynamics simulations, were then rationalized in terms of the structure of the potential energy surface. In this paper we report on the phase behavior of the (KCl)₃₂ cluster. However, because the potential energy surface is too complicated to study in microscopic detail, (KCl)₃₂ was examined by a statistical approach. The statistical approach consists of a method to estimate the density of configurational states as a function of energy, from which, the partition function of (KCl)₃₂ can be obtained in a form that explicitly takes into account the potential energy surface.

2. Method

(KCl)₃₂ was studied by a combination of techniques: constant energy and constant temperature molecular dynamics (MD), potential energy surface minimizations, and simple statistical mechanical theory. The intention of the statistical approach was to derive an expression for the density of configurational states which could be evaluated using simulation data as the input.

The velocity form of the Verlet propagation algorithm [2] with a time step of 3×10^{-15} seconds was used to calculate the constant energy MD trajectories. The Nosè [3] method was used for the constant temperature MD and a sixth-order Gear predictor-corrector [4] algorithm with a time step of 2.5×10^{-15} seconds was used to integrate the constant temperature equations of motion.

Minima on the potential energy surface were located using either the steepest-descent or conjugate gradient minimization technique. The conjugate gradient method was preferred because it is more efficient for large systems.

The Born-Mayer type interaction potential used for this study is the same one used previously to model (KCl)₄ and (KCl)₅ [1]:

$$\Phi = \sum_{i < j} \Phi_{ij} = \sum_{i < j} \left[\frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-r_{ij} / \rho) \right]. \quad (1)$$

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The values of the constants A_{ij} ($A_{++} = 1555.21$ eV, $A_{+-} = 1786.91$ eV, $A_{--} = 1924.80$ eV) and ρ (0.337 Å) are those given by Tosi and Fumi [5].

3. Results

The most stable isomer of $(\text{KCl})_{32}$ is a $4 \times 4 \times 4$ rocksalt-like structure with energy $\phi = -3.3703$ eV/ion. The lowest energy excited state is a $3 \times 4 \times 4$ rocksalt-like structure with the four remaining ions situated in a line parallel to an edge of the parallelepiped. This crystal-like structure has an energy of $\phi = -3.3534$ eV/ion creating an energy gap Δ of 0.017 eV/ion. We assume that above the energy gap the density of stable configurational states, $G(\phi)$, is a continuous function of the quenched energy ϕ .

We found it useful to separate the locally stable structures of this cluster into three categories. The first category consists of crystal-like structures that are mostly regular and rocksalt-like except for a few defects. The second category includes what we call nonwetted structures; structures that are partly regular, rocksalt-like and partly highly disordered. The last category contains a very large number of minima that have completely disordered (amorphous) configurations. In Fig. 1 we show examples of the nonwetted and amorphous structures. On average the crystal-like structures are lowest in energy, the nonwetted structures intermediate, and the amorphous structures highest in energy. The nonwetted structures are particularly interesting as they represent behavior that has not been observed in rare gas clusters.

Extensive MD simulations revealed that $(\text{KCl})_{32}$ has distinct solid-like and liquid-like phases. The transition between the two phases appears to be sharp in the sense that (1) the melting event, as it occurs during a single MD trajectory, is well-defined and abrupt and (2) during a particular MD trajectory, if the cluster transforms from the solid-like phase to its liquid-like phase it rarely, if ever, transforms back to its solid-like phase. Hence, we were unable to find any evidence for sustained dynamic coexistence of solid-like and liquid-like forms of $(\text{KCl})_{32}$. This result contrasts with Ar_{13} and Ar_{55} in which a dynamic solid/liquid coexistence is manifested by abrupt, well-defined transitions between the solid-like and liquid-like forms of the cluster. The failure of $(\text{KCl})_{32}$ to exhibit any semblance of sustained dynamic phase coexistence on the nsec time scale of our simulations is either a consequence of a sharp dependence of the [liquid]/[solid] equilibrium ratio on the temperature, a very long time scale for passage between the solid-like and liquid-like phases, or a combination of these two effects.

The identification of the most stable isomer, the lowest energy excited state with attendant energy gap Δ , and classification of the locally stable structures into three categories is about as precise as we can expect to map out the potential energy surface of $(\text{KCl})_{32}$. The microscopic approach we used for $(\text{KCl})_4$ and $(\text{KCl})_5$ is simply not possible for $(\text{KCl})_{32}$. Instead we assume a statistical approach in which we can still, albeit in a much less precise way, relate the thermodynamics of the cluster to its potential energy surface. We accomplish this by calculating the function $G(\phi)$ and then writing a partition function $Z(\beta)$ for $(\text{KCl})_{32}$ that explicitly depends on $G(\phi)$. From $Z(\beta)$ we can estimate the

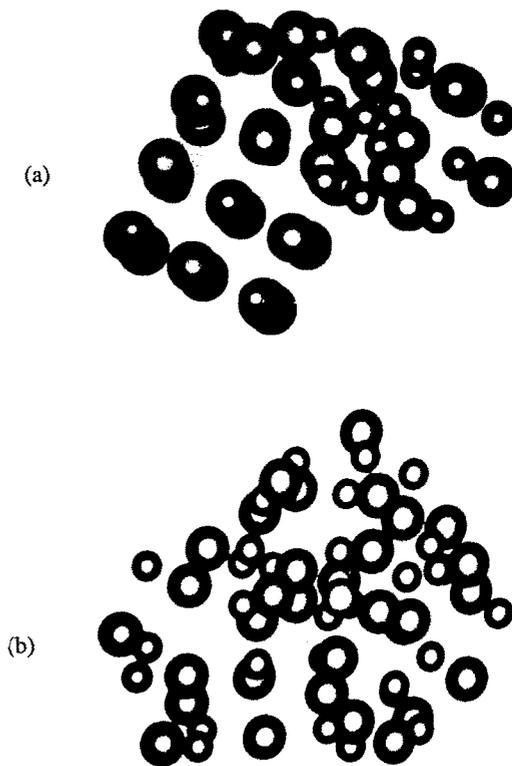


Fig. 1. (a) nonwetted structure, $\phi = -3.3254$ eV/ion and (b) amorphous structure, $\phi = -3.2993$ eV/ion.

thermodynamic properties of the cluster while $G(\phi)$ provides us with the desired connection to the potential energy surface.

The density of configurational states, $G(\phi)$, is defined so that $G(\phi)d\phi$ is the total number of locally stable structures with quenched energy ϕ in the energy range $d\phi$ around ϕ . We can express $G(\phi)$ mathematically in the following form

$$G(\phi) = \frac{P(\phi, \beta') Z_t(\beta')}{e^{-\beta' \phi} Z_{vib}(\phi, \beta')} \quad (2)$$

$P(\phi, \beta')$ is the normalized probability that the cluster will be found vibrating around a locally stable structure with equilibrium energy ϕ , at inverse temperature β' . $Z_{vib}(\phi, \beta')$ is the vibrational partition function of any locally stable structure with equilibrium energy in the range $\phi \pm \frac{d\phi}{2}$ at inverse temperature β' . Finally, $e^{-\beta' \phi}$ is a Boltzman factor and $Z_t(\beta')$ is the value of the total partition function at β' (basically just a normalization constant). Note that β' refers to a specific value for the inverse temperature.

The evaluation of $G(\phi)$ amounts to the calculation of $P(\phi, \beta')$, $Z_{vib}(\phi, \beta')$, and $Z_t(\beta')$. These quantities can be determined from MD simulations coupled with potential minimizations. The actual details of the calculation of these quantities are given elsewhere [6] and will not be repeated here.

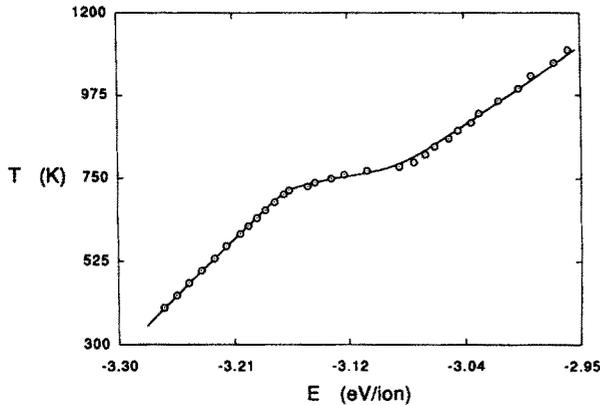


Fig. 2. Constant temperature caloric curve; points are MD simulation data and the solid line is the fit using the statistical model.

If we can evaluate $G(\phi)$ as a function of ϕ then we can substitute it into the following expression for the partition function of $(\text{KCl})_{32}$

$$Z_i(\beta) = \frac{e^{-\beta\phi} Z_{vib}(\phi, \beta)}{\sigma(\phi_g)} + \int_{\phi_l}^{\phi_u} \frac{e^{-\beta\phi} Z_{vib}(\phi, \beta) G(\phi)}{\sigma(\phi)} d\phi; \quad (3)$$

where ϕ_g is the energy of the ground state and $\sigma(\phi)$ is the symmetry number of a structure with equilibrium energy ϕ . The first term on the right hand side of Eq. 3 represents the partition function for the ground state structure and was extracted from the integral to account for the energy gap Δ . To demonstrate the accuracy of this method we compare in Fig. 2 the caloric curve calculated from our statistical model with that computed by constant temperature MD. The goodness of the fit depends on the values of two free parameters which can be determined easily by a trial and error process.

One noteworthy thermodynamic quantity that we can estimate from our partition function is $P(\phi_g, \beta)$. $P(\phi_g, \beta)$ is the probability, at β , that $(\text{KCl})_{32}$ will be found vibrating around its rocksalt-like ground state configuration. (Probability is defined here, in terms of a canonical ensemble of $(\text{KCl})_{32}$ clusters.) Based on the results of MD simulations we identify $P(\phi_g, \beta)$ with the fraction of solid-like clusters in a canonical ensemble of $(\text{KCl})_{32}$ clusters. In Fig. 3 we show $P(\phi_g, \beta)$ as a function of temperature. Notice the significant range of temperatures within which measurable quantities of the solid-like and liquid-like forms of $(\text{KCl})_{32}$ can coexist. For bulk KCl $P(\phi_g, \beta)$ would be a step function at the bulk melting temperature. The rounding of $P(\phi_g, \beta)$ for $(\text{KCl})_{32}$

is a quintessential example of the effects of finite-size on phase behavior.

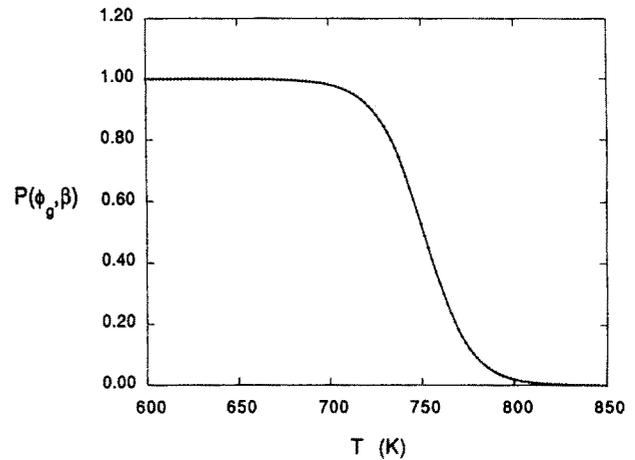


Fig. 3. $P(\phi_g, \beta)$ as a function of temperature. See text for details.

4. Discussion

In this paper we reported on the structural behavior of the $(\text{KCl})_{32}$ cluster, notably, “nonwetting” structures that are partly ordered, rocksalt-like and partly highly disordered—these types of structures have not been observed in rare gas clusters. We also reported on the phase behavior of $(\text{KCl})_{32}$. Extensive MD simulations revealed no substantial evidence for a dynamic coexistence of solid-like and liquid-like forms of $(\text{KCl})_{32}$. However, from our statistical model we found that there is a significant range of temperatures within which the solid-like and liquid-like forms of $(\text{KCl})_{32}$ can coexist. These apparently conflicting results can be reconciled by postulating that, the time scale for passage between the two phases of $(\text{KCl})_{32}$, is beyond the time limits of reasonable length MD trajectories.

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