The Possibilities for Glassy Clusters: (KCl)$_{32}$

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Abstract. The (KCl)$_{32}$ cluster is used as a model system to study the possibilities for clusters to exhibit amorphous or glassy solid forms. The problem has two aspects: first, whether the potential surface of the cluster supports a myriad of locally stable, disordered structures, the ensemble of which would constitute the glassy state, and second, whether an ensemble of amorphous clusters can be prepared under laboratory conditions. Molecular dynamics studies give an emphatic *yes* to the first issue, and an equally emphatic *no* to the second, for cooling rates up to 10^{12} K/s, a thousand-fold faster than the fastest rates yet reported. However, if the long-range Coulomb interaction of the ions is replaced by a shielded Coulomb (Debye or Yukawa) potential, the secondary minima are sufficiently stabilized and the saddles, sufficiently high, that disordered equilibrium structures can be reached by cooling at fast, but still conceivably attainable rates. The implication is that while alkali halide clusters probably cannot form glasses, binary clusters with shorter-range forces, such as those of II-VI and III-V compounds, probably can form glasses. The highly disordered structures of (KCl)$_{32}$ are perhaps the most disordered forms yet seen for solid matter.

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1. Introduction

Clusters exhibit many locally stable structures, their number probably increasing exponentially with N, the number of particles in the cluster [1-3]. Many of these are, inevitably, more or less disordered [4]. This observation leads inevitably to the question of whether clusters can be prepared in disordered, amorphous or glassy form. Stillinger [5] has found it useful to classify the locally stable structures of a system into two sets, amorphous and crystalline. For (KCl)$_{32}$ we have used as many as four categories: (1) the unique structure of the global minimum (2) mostly

ordered structurs with only a few defects (3) the structures we have called "non-wetting", which are regular in one part and disordered in the other and (4) the entirely amorphous structures [6]. The entirely disordered structures we have found for alkali halide clusters, including (KCl)$_{16}$ and the principal vehicle for this paper, (KCl)$_{32}$, are very disordered indeed—possibly more so than any other form of condensed matter. For the most part, these structures show little or no short-range order, in contrast with conventional bulk glasses, which can exhibit substantial short-range order. We propose to describe an ensemble of clusters whose structures are distributed among these highly disordered forms as being in a micro-amorphous state. A collection of clusters, physical or simulated, representable as being in a micro-amorphous state, is appropriately called "glassy". (Collections of clusters large enough to have no long-range order but some short-range order might also turn out to fit conveniently under the definition of "glassy". Alternatively, if their properties differ from those of micro-amorphous clusters, it will be useful to distinguish the two kinds of clusters. We do not consider such large clusters, presumably with N of order 10^6 or 10^9, in this analysis.)

If a cluster can exhibit a glass-like state, it must have a number $G(\phi)$ of locally stable disordered configurations ("inherent structures") whose energies lie in the energy band $d\phi$ around each energy ϕ, down to some minimum, into which it may be trapped. Generally, at energies well above that of the global minimum, this number is very large, much larger than the number of mostly ordered structures in the same energy range. Hence statistical weights of the numbers of minima favor overwhelmingly the formation of disordered structures. However, the densities of locally stable states, which can now be estimated and classified for clusters of moderate size [6], are still not sufficiently large to ensure that a kind of cluster will form a glass. The question rests not only on the numbers of minima but also on both the shape of the potential surface—the hyperareas (or microcanonical entropies) of the basins above each minimum and the heights and accessibilities of the saddles separating the wells—and the means by which the energy or temperature of the clusters is reduced to achieve

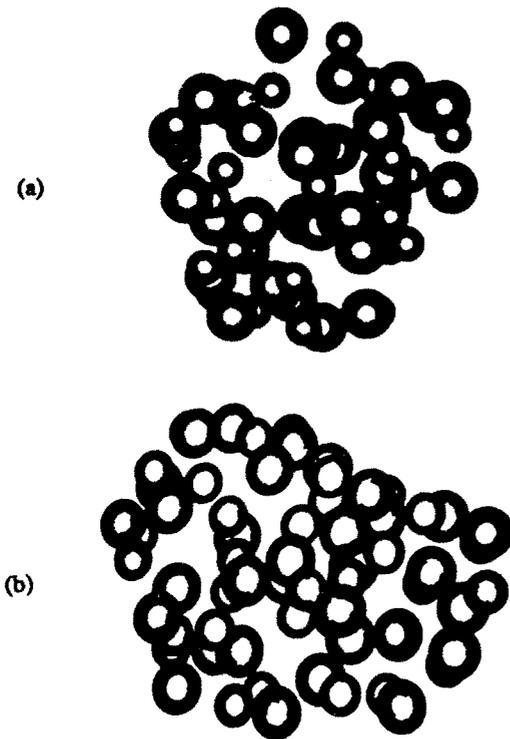* Department of Chemistry, The University of Oregon, Eugene, Oregon 97403, USA

(a)

(b)

Fig. 1. (a) amorphous structure from instantaneous quenching using un-shieleded potential and (b) amorphous structure from cooling using shielded potential. See text for details.

a "frozen" state, whether glassy or regular. This paper is a brief discussion of just this issue, of the conditions for the formation (or non-formation) of glassy clusters; a fuller discussion will appear [7].

We use binary, salt-like clusters for this study; specifically we use $(KCl)_{32}$ represented by a Coulomb-plus-exponential repulsion (Born-Mayer) potential, and a hypothetical $(MX)_{32}$ cluster represented by a similar potential with the Coulomb interaction replaced by an exponentially shielded Coulomb (Debye or Yukawa) potential with range and depth adjustable. The potential is

$$\Phi = \sum_{i<j} \left[B e^{-(\gamma_i+\gamma_j)r_{ij}} \frac{q_i q_j}{r_{ij}} + A_{ij} \exp(-r_{ij}/\rho) \right]; \qquad (1)$$

with q_i, q_j the charges on ions i and j and r_{ij} the distance between them. The repulsion parameters [8] are $A_{++} = 1555.21$ eV, $A_{+-} = 1786.91$ eV and $A_{--} = 1924.80$ eV and we have taken $\rho = 0.337$Å. For $(KCl)_{32}$ itself, $B = 1$ and $\gamma_i = \gamma_j = 0$; for general $(MX)_{32}$, various values of these parameters were tried. Simulations at constant energy of $(KCl)_{32}$ and its shielded counterparts were carried out with the velocity form of the Verlet algorithm [9] with a time step of 3×10^{-15} seconds. Constant-temperature simulations were conducted with the Nosé Hamilitonian dynamics [10,11] propagated by a sixth-order predictor-corrector algorithm [12] with a time step of 2.5×10^{-15} seconds.

2. $(KCl)_{32}$: Theoretical and Real Glassy States

The $(KCl)_{32}$ cluster conforms to the "magic number" condition for alkali halides, that is, it forms a $4 \times 4 \times 4$-particle rocksalt cube—the structure of its global energy minimum. It also has a number of stable structures that are clearly rocksalt-like but with a few defects, many stable structures that have some rocksalt-like structure and some amorphous character (these structures show how liquid alkali halides do "not wet" their solids uniformly), and very many highly disordered structures with no discernible rocksalt-like character. One such amorphous structure is shown in Fig. 1a. These structures have been found by carrying out constant-energy molecular dynamics simulations and quenching [13,14], i. e. removing the kinetic energy of the simulated cluster and then following its potential surface directly downward to the local energy minimum. Physically, the procedure corresponds to instantaneous freezing, with no thermal atomic motion at all, from the instant the molecular dynamics is momentarily stopped. In the energy range in which amorphous structures are found, about -3.31 eV/ion or more, there are of order 10^{12} amorphous structures for each "crystalline" rocksalt-like structure.

The degree of order can be given quantitative meaning through the radial distribution (RDF), for example [6,7]. The RDF of the global minimum structure is essentially the same as that of rocksalt itself while tthat of any of the disordered structures is a bumpy approximation to that of liquid $(KCl)_{32}$. The RDF constructed by averaging the RDFs of 8 disordered structures is essentially the same as that of liquid $(KCl)_{32}$. These are shown in Fig. 2.

Instantaneous quenching clearly generated a collection of structures that represent a theoretical glassy state for $(KCl)_{32}$. Not only are the variety of disordered structures and the degree of their disorder consistent with the conditions for glassy clusters, even the shortness of the interval required to pass from one well to another, as little as 20 steps, is consistent with the notion of glassy clusters. In fact, the equilibrium structures of different wells reached from trajectory points only 20 time steps apart are frequently dramatically different. But despite the capacity of $(KCl)_{32}$ to form theoretical glasses, all fixed-energy simulations of cooling at finite rates—even at 10^{11} K/s—produced either the global minimum structure or other rocksalt-like structures. Cooling at about 10^{13} K/s was required to yield amorphous structures, consistent with early results for $(KCl)_{256}$ based on a somewhat different potential [15]. These results imply the striking result that $(KCl)_{32}$ anneals in no more than 10 vibrational periods but, to no major surprise, cannot anneal in 1/10 of a vibration.

3. $(KCl)_{32}$ Analogues: Theoretical and Real Glassy States

Analogues of $(KCl)_{32}$ with shielded Coulomb potentials were simulated with constant-energy stages of cooling. For simplicity we set $\gamma_i = \gamma_j = \gamma$ in the interaction potential. For three of the cases studied, ($B = 1.288, \gamma = 0.065$Å^{-1}; $B = 1.482, \gamma = 0.1$Å^{-1}; and $B = 4.713, \gamma = 0.375$Å^{-1}),
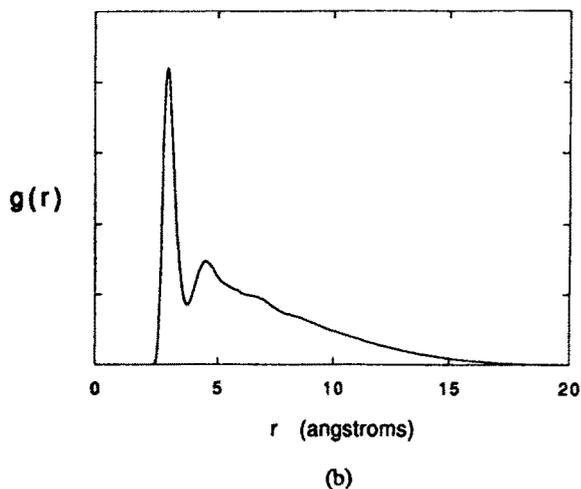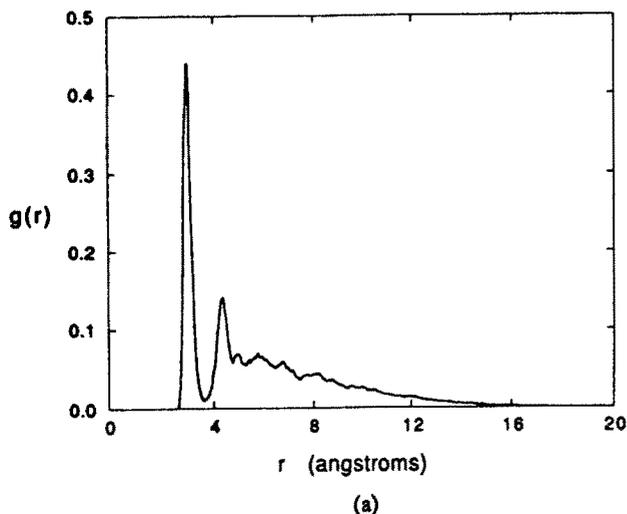
(a)

(b)

Fig. 2. (a) Radial distribution function (RDF), average of eight RDF's of amorphous structures from instantaneous quenching using unshieleded potential and (b) RDF of liquid

minima into the multidimensional potential [16-18] and increasing the height of barriers. It is reasonable to infer that the parameters of the fourth case are sufficient to permit the corresponding hypothetical clusters to form glasses, not yet under conditions attainable in the laboratory, but at least under conditions with a semblance of realism. This in turn shows not only what qualitative features the multidimensional potential must have if the system is to be capable of glass formation; it also begins to reveal the quantitative nature of those characteristics. With this information, it is now possible to tune the parameters to find the precise dependence of the well depths and barrier heights required to allow glass formation at any desired cooling rate. The potential surface of a "good" glass former can then be compared to the surface of a "poor" glass former to identify the operative characteristics of glass formation.

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only crystal-like structures were obtained, even at cooling rates of 10^{11} K/s, showing that such clusters cannot form glasses under realistic conditions. However, with $B = 5.818, \gamma = 0.375\text{Å}^{-1}$, cooling at approximately 5×10^{11} K/s did yield glassy-like structures such as that of Fig. 1b. Shortening the range of the long-range part of the pair interaction has the effect of putting more high-energy local