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Mapping the global minima of binary Morse clusters: The effects of range mismatch

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ABSTRACT

The putative global minima of binary Morse clusters have been systematically determined using the parallel basin-hopping method. Clusters $A_{n_A}^{(\alpha)}B_{n_B}^{(\beta)}$ with a total size $n_A + n_B$ ranging between 5 and 55 atoms were studied for all (n_A,n_B) compositions, using a simple arithmetic combining rule for the range of the potential between unlike elements. Several order parameters are evaluated in order to characterize the global minima and to identify remarkable individuals. The stable structures generally show some phase separation with the long-range element surrounded by the short-range element, but some degree of mixing is found as well in order to minimize the overall strain. All clusters exhibit icosahedral features, except at the total size of 38, where depending on the range and composition truncated octahedra are found.

1. Introduction

Among atomic and molecular clusters, binary clusters of chemically similar elements have recently attracted a lot of attention, owing to the possibilities offered by tuning the composition in addition to size. Mixing elements at the nanoscale is particularly promising for metals, especially as concerns with applications in optoelectronics or catalysis [1]. At a more fundamental level, the simpler bonding of the rare gases has made them appealing systems to understand the factors responsible for the variety of observed behaviors ranging from full mixing (alloying) to phase separation [2]. These factors are generally thought to predominantly include the size mismatch and the difference in surface energies, however the kinetics may be of importance as well [1].

Binary clusters also pose a challenge to theoreticians, due to the greater complexity of their potential energy landscapes arising from the presence of the so-called homotops [3], or structures that differ only in their chemical ordering. This complexity has lead to a wealth of investigations aimed at characterizing the properties of mixed clusters bound by simple potentials, typically of the embedded-atom model (EAM) family for metals [4–10], or by Lennard–Jones (LJ) pair potentials for the rare gases [11–17].

Besides the equilibrium distance and well depth, the range is a defining feature of an interatomic potential with a strong influence on structural [18–20], thermodynamical [21–23], and kinetic [24,25] properties. Short-range potentials, which are found e.g. in colloids [26,27] or in molecular clusters such as C_{60} [28], tend to favor close packing and destabilize liquids in favor of sublimation [21]. In striking contrast, long-range potentials are more relevant to interactions involving delocalized electrons or polarization effects, as in metals, and produce more disordered geometrical patterns with higher coordination [29] and a greater resistance to thermal dissociation [30]. The effects of the potential range on the structure of clusters have mostly been addressed for homogeneous systems bound by shielded Coulomb [31,32] or Morse [18,19,29,33,34] potentials. Binary clusters of Morse particles have been studied by Parodi and Ferrando [35] who focused on the specific size of 38 known to possibly exhibit fcc-like structures [18].

In the present contribution, we extend this effort by systematically addressing the most stable energy minima of binary Morse clusters containing up to 55 atoms, for all compositions and for three sets of ranges. This work complements previous studies on bimetallic clusters [6,36] in which the influence on the stable cluster structures of the parameters of the heteronuclear interactions, including the range, was systematically addressed. Here, our analysis is based on several order parameters that are suited to illustrate various features of the global minima, including geometric properties such as the moments of the gyration tensor or the bond-orientational order, the extent of chemical order through mixing order parameters, and the energetics of mixing. Our results generally show that mixed clusters are strongly phase separated in a core/shell fashion, and that icosahedral order is favored, even for short-range potentials. In agreement with Parodi and Ferrando

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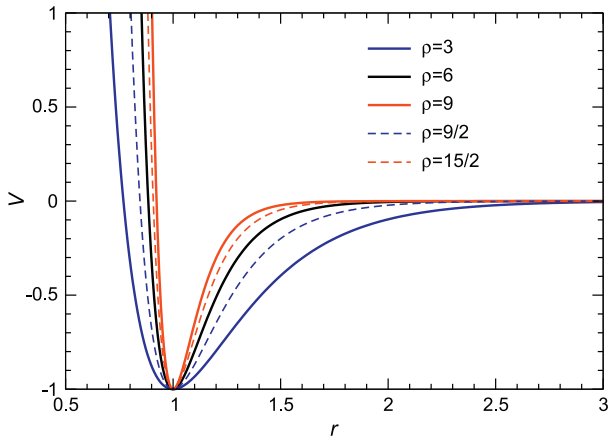

Fig. 1. Morse potential for various ranges ρ, as used in the present model of binary clusters.

[35], we also find that mixing different Morse particles destabilizes octahedral order in the 38-atom clusters depending on range and composition, rather than stabilizing this order in other sizes.

The article is organized as follows. In the next section, we briefly describe the system under study and the methods used for global optimization. The results are presented and discussed in Section 3, before some concluding remarks are given in Section 4.

2. Model and methods

Depending on its range, the Morse potential [37] is able to mimic the interaction between various atoms or even molecules. For a binary cluster $A_{n_A}B_{n_B}$ with Cartesian coordinates $\{\mathbf{r}_i, i = 1 \cdots n_A + n_B\}$, we write the total interaction energy as

$$V(\{\mathbf{r}_i\}) = \sum_{i<j} \varepsilon_{ij} e^{\rho_{ij}\left(r_0^{(ij)} - r_{ij}\right)} \left(e^{\rho_{ij}\left(r_0^{(ij)} - r_{ij}\right)} - 2 \right), \quad (1)$$

where ε_{ij} is the well depth, $r_0^{(ij)}$ the equilibrium distance, and ρ_{ij} the range associated with the pair interaction between particles i and j. There are three types of interactions in our binary systems, involving A–A, B–B, and A–B pairs. Our purpose is to focus on the effect of the range ρ_{ij}, hence we choose to take the well depths ε_{ij} and equilibrium distances $r_0^{(ij)}$ to be identical for all pairs, and taken both as unity. For the ranges, we have used the simple arithmetic combining rule $\rho_{AB} = (\rho_{AA} + \rho_{BB})/2$ already adopted by Parodi and Ferrando [35].

The LJ potential is approximately equivalent to $\rho = 6$, and this is commonly accepted as a medium-range interaction, whereas $\rho = 3$ and $\rho = 9$ are indicative of long- and short-range interactions, respectively. We have thus considered the three following sets of range parameters to define the mixed systems: $(\rho_{AA},\rho_{BB}) = (3,6)$, (3,9), or (6,9), and in all cases A atoms have a longer-ranged potential than B atoms. We note that those values span a broader interval than the values used by the authors of Ref. [35], who were more interested in modeling the behavior of metals. The variations of the Morse potentials for $\rho = 3$, 4.5, 6, 7.5, and 9 are depicted in Fig. 1 as a function of interparticle distance. For the sake of notations, we will thereafter denote as $A_{n_A}^{(\alpha)}B_{n_B}^{(\beta)}$ the cluster $A_{n_A}B_{n_B}$ in which $\rho_{AA} = \alpha$ and $\rho_{BB} = \beta$.

Putative lowest-energy structures were located using a parallel extension [14] of the basin-hopping algorithm [38] with ideas borrowed from parallel tempering Monte Carlo [39]. In this method, each replica is assigned a fixed composition, and random moves are performed altering either the global geometry of the

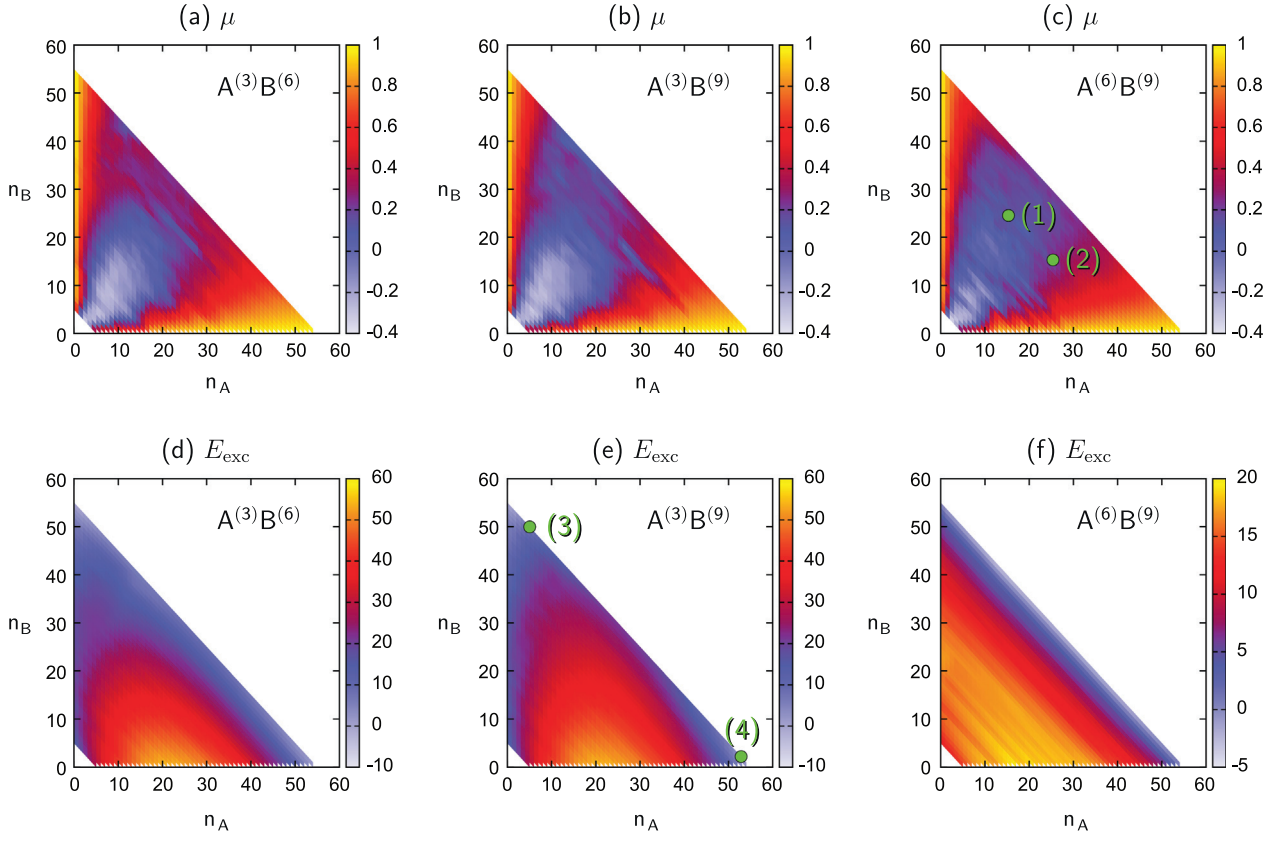

Fig. 2. Two-dimensional map of (a–c) the mixing parameter μ; and (d–f) the excess energy E_{exc}, for $A_{n_A}^{(\alpha)}B_{n_B}^{(\beta)}$ clusters as a function of n_A and n_B, for ranges (α,β) of (a,d) (3,6); (b,e) (3,9); (c,f) (6,9). Green dots and numbers indicate particular structures that are depicted in Fig. 9. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)