Contents lists available at ScienceDirect

Chemical Physics Letters

Unveiling the mechanism of core–shell formation by counting the relative occurrence of microstates

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ARTICLE INFO

ABSTRACT

A procedure usually applied to construct free energy surfaces for a system at equilibrium is found here useful for obtain information on a non-equilibrium process. The joint probability of observing collective variables from a swarm of irreversible molecular dynamic trajectories is analyzed. This straightforward procedure can supply detailed mechanistic information on the irreversible coalescence of two particles made of 42 Au atoms and 13 Co atoms respectively. A complex mechanistic behavior is unveiled using the analysis proposed. This is performed without the need to compute large databases containing minima and transition rates, as required by master equation methods.

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1. Introduction

The problem of nanoparticle (NP) coalescence is a hot research area, since this method has been employed [1–4] or proposed [5–9] for the controlled preparation of bimetallic nanoparticles (BNP), which can be used for multiple applications, ranging from medicine to catalysis [7]. Yacaman et al. have shown that the mobility of the surface layers of the nanoparticles plays an essential role in particle coalescence [4]; they have also analyzed the case of homoatomic particles by means of molecular dynamics simulations [3]. Very recently, different research groups have shown a number of remarkable features occurring in core–shell nanoparticles, giving a renewed impetus to research in this area [10–15]. In the present Letter we show that the mobility of surface atoms plays a particularly important role in limiting the formation of the equilibrium structure of a core–shell prepared from cluster coalescence. With this purpose, a novel approach is proposed for the analysis of the results of non-equilibrium molecular dynamics simulations.

The Landau free energy surface (FES) has been found very valuable to study equilibrium properties of numerous systems [16,17]. The FES of a system may be written as

$$F(Q_1, \ldots, Q_n) = -kT \ln P(Q_1, \ldots, Q_n) + const \qquad (1)$$

where $P(Q_1, \ldots, Q_n)$ is the joint probability of observing the $Q_1, \ldots, Q_n$ values for a set of n order parameters or collective variables (CVs) in the canonical ensemble of the system. The CVs collect together different system states in an arbitrary n dimensional space.

Here, "microstate" will be referred to as the set of states that are grouped around the same region in the CV space [18].

The FES is commonly explored using computer simulations to study different configurations with its corresponding population for systems close to equilibrium. In the condensed matter area, Lynden-Bell and coworkers have used a FES construction to study transition-phase phenomena in metal clusters [19–21]. They calculated Gibbs free energy differences and analyzed metastable states in the coexistence between liquid and solid phases. These studies also brought insight into the connection between the FES and thermodynamic properties of different ensembles, in addition to the canonical one. FESs have also been found useful for studying nucleation and growth of metal NPs [22,23].

2. Model and methods

Different computational methods (e.g. umbrella sampling [24], hyperdynamics [25], metadynamics [26–28], and many others [29–31]) allow improving the FES/PES (potential energy surface) sampling. If transition rates between different minima on these surfaces are estimated, master equation dynamics [32] can be used to study dynamic properties and the kinetics of the system. In this respect, a major advance was made by Wales and coworkers with the implementation of the discrete transition path method [33–38,33]. Wales and Evans used this methodology to analyze the approach to equilibrium of a small peptide starting from an artificial distribution [35].

For the discussion below, we will define the frequency of microstate occurrence $P\prime(Q_1, \ldots, Q_n)$ as the joint probability of observing the CVs $Q_1, \ldots, Q_n$ in an arbitrary set of straightforward molecular dynamics (MD) simulations carried out in the canonical ensemble.

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If these MD trajectories were representative of the equilibrium state of the system, then this frequency would correspond to the probability P, and the FES could be obtained through Eq. 1. This would be the direct way to construct the FES. In this Letter, we will show that, although the set of trajectories used to construct P' is out of equilibrium, this quantity provides useful information on a dynamic process, in the present case, heteroatomic NP coalescence. Here, P' is certainly not related to the canonical probability density; using it in Eq. 1 will clearly not give the FES of the system. However, as shown below, important information regarding a non-equilibrium process can be extracted. Furthermore, this information is derived without the need of the computation of large databases containing minima and transition rates as needed by master equation methods. Only a swarm of molecular dynamics trajectories, starting from some general defined initial condition associated with the non-equilibrium process under consideration, is needed.

To evaluate the usefulness of P' to study an irreversible process, we consider the coalescence process of two NPs made of 42 Au atoms and 13 Co atoms respectively. We set the initial condition for this process as follows: by denoting with x the axis joining the centers of mass of both nanoparticles, the NPs were initially separated by setting the smallest Δx component of all the Au–Co distances equal to 5 A (see Figure 1). Then, a total of 256 molecular dynamics simulations runs were started from this condition with different random seeds. For each of them, the relative initial orientations of the NPs were randomized. Therefore, the simulations will lead to a swarm of trajectories starting from the previously described simulation conditions.

The metal interatomic interactions were modeled using the second-moment approximation of tight-binding (the parameters were taken from reference [11]). The integration of the motion equations was made at a constant temperature of 550 K using the Ermak algorithm with a viscosity of 5 ps^{-1}. To get the swarm of trajectories mentioned above, each trajectory was launched using a different sequence of random numbers, which was assigned following the parallel random sequences scheme of Numerical Recipes [39]. From the 256 total simulation, 14 trajectories were discarded since they increased nanoparticle separation. The other 242 led to the coalescence process; system configurations were recorded every 500 ps. Figure 1 shows representative snapshots at different stages of coalescence. As it can be seen in the picture, the final state is an icosahedral bimetallic core–shell nanoparticle (BNP) with Au in the shell and Co in the core.

3. Results and discussion

The time elapsed needed to the get the final coreshell structure was registered for each trajectory. The histogram of these waiting times is plotted in Figure 2. Two maxima are evident in this figure showing a non-trivial mechanism for the process. To understand
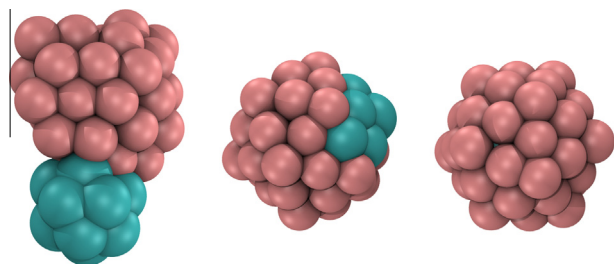

Figure 2. Distribution of waiting times needed for the formation of the final core–shell structure. The occurrence of two maxima evidences a non-trivial kinetics.

the nature of these peaks, we selected a CV and analyzed the frequency of microstate occurrence P' arising from the trajectories. A suitable CV must take different values as the process develops. In the present case, we chose the distance between the centers of masses of the two species (d_{CM}), since this parameter can distinguish between initial and final state and it passes through intermediate values during the process. Therefore, each state having similar values of d_{cm} defines a microstate. The simulations were stopped when the condition $d_{CM} < 0.03$ Å (tested each 500 ps) was fulfilled. Figure 3a shows $P'(d_{CM})$ in energy units. This is certainly not the Landau free energy, since the trajectories are not
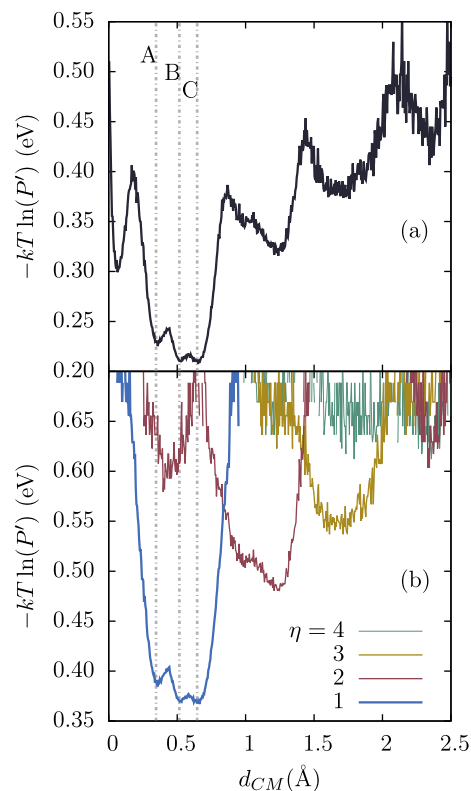
Figure 3. (a) Logarithm of the frequency of microstate occurrence (multiplied by kT) as a function of the distances between the center of masses of the clusters d_{CM}, used here as a collective variable. A movie was built running over the configurations employed to construct this plot (see Supplementary Information). (b) Similar to (a), however, the frequencies have been partitioned into the different number of Au atoms (η) in the core of the nanoparticle.

Figure 1. Snapshots of the system taken during the coalescence process. Au atoms are shown in pink and Co atoms in blue. (For interpretation of the references to color in this figure legend, the reader is referred to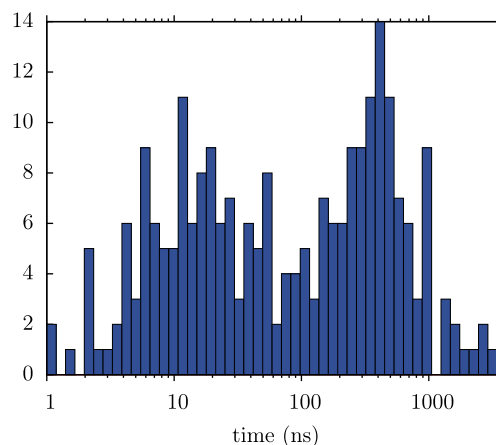 the web version of this article.)