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Evidence for broken ergodicity due to chemical alloying from the dissociation kinetics of binary clusters

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The interplay between thermal relaxation and statistical dissociation in binary Morse clusters $(AB)_N$ has been investigated using numerical simulations and simple statistical approaches, for a variety of interaction parameters covering miscible and non-miscible regimes. While all clusters exhibit a core/shell phase separation pattern in their most stable, $T = 0$ structure, different melting mechanisms are identified depending on the ranges and their mismatch, including two-step melting of the surface and the core or premelting as alloying. The preference for emitting A or B particles upon evaporation has been evaluated assuming that the cluster is either thermally equilibrated or vibrationally excited in its ground state structure, and compared to the predictions of the Weisskopf theory. The variations of the dissociation rate constants with increasing energy and the branching ratio between the two channels show significant differences in both cases, especially when the clusters are miscible and bound by short-range forces, which indicates that the time scale for evaporation is much shorter than the equilibration time. Our results suggest that dissociation properties could be used to test the ergodic hypothesis in such compounds. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4880277>]

I. INTRODUCTION

Statistical mechanics at equilibrium often implicitly relies on the ergodic hypothesis, which states that a dynamical system visits phase space in such a way that time and ensemble averages coincide. It is usually impossible to demonstrate that ergodicity has been achieved in a realistic system, however practical situations of non-ergodicity can be numerically demonstrated using dedicated probes.¹ In practice, broken ergodicity results from kinetic trapping in distant parts of the energy landscape that are connected by high energy barriers,² and can be alleviated in simulations by a variety of algorithms such as flat-histogram methods,^{3,4} replica exchange,^{5,6} or auxiliary use of approximate densities of states.⁷

The difficulty in questioning the ergodic hypothesis is mainly due to the necessity of producing truly equilibrated averages to serve as a benchmark, deviations to these averages being a direct indication of non-ergodicity. Indirect evidence for ergodic behavior must be searched in properties that are sensitive to statistical quantities, themselves depending on equilibration. Thermal dissociation of finite clusters offers such an opportunity, as the related observables of rate constants or kinetic energy released are intimately connected to the statistical properties through the densities of states (DOSs).^{8,9} Earlier investigations on small rare-gas^{9,10} or metallic¹¹ clusters have shown that statistical rate theories can be made accurate against numerically exact molecular dynamics simulations if the densities of states are carefully evaluated including anharmonicity effects. In those works, the residual discrepancies could be attributed to the poor knowledge of the absolute DOSs, rather than manifestations of non-ergodicity.⁹

Morse clusters are particularly interesting in the context of thermal dissociation, because the stability of the liquid state strongly depends on the range of the interaction.¹² In particular, in the short-range (hard-sphere) limit particles tend to sublime instead of melting altogether.¹³ Clusters bound by the Morse interaction exhibit a broader variety of structures than the commonly studied LJ clusters, because the range of the potential directly influences the coordination particles can sustain while also inducing some collective strain in the stable packings.^{14,15} Beyond the stable structures, the range of the Morse interaction alters the entire energy landscape,^{16–18} hence the equilibrium properties,^{19–21} and global relaxation kinetics.²²

For homoatomic clusters, broken ergodicity takes place notably in presence of multi-funnel energy landscapes causing structural transitions at low temperature.^{2,7,23,24} However, ergodicity may be further hindered by the even more complex landscapes of heterogeneous clusters of unlike elements, due to the various types of chemical ordering they can exhibit depending on the details of the interactions. This additional complexity arising from mixing elements has been explored in metallic nanoalloys²⁵ but also in binary Lennard-Jones (LJ) compounds.^{26–32} Its influence on the relaxation kinetics³³ suggests that binary clusters could be suitable candidates for addressing the fundamental issue of ergodicity, at least in the case where broken ergodicity reflects failure of equilibrating chemical order. One further benefit of dealing with heterogeneous clusters in the context of thermal dissociation is the possibility to exploit the branching ratio as the main observable, a more readily accessible property in experiments.

The stable structures of binary Morse clusters of particles with different ranges, say A with B, generally exhibit a core/shell phase separation pattern with the long-range bound

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particles A coated by the short-range bound particles B.^{34,35} Although the finite temperature dynamics of such clusters remains undocumented, it would seem intuitive that B particles, lying outside and being less stable in the liquid phase, would evaporate before A particles upon heating. However, especially at low temperatures dissociation may compete with isomerization and relaxation. Depending on the ranges and their mismatch, various situations can be anticipated in which the core/shell phase remains the free energy minimum at finite temperature, or be supplanted by a more mixed phase stabilized by entropy.³⁶ It is unlikely that such randomly alloyed phases would thermally decay in similar proportions as their phase separated counterpart, and those differences provide us with a means of testing the ergodic hypothesis through the dissociation observables.

In the present article, we address those issues by getting insight into the finite temperature properties of binary Morse clusters at and out of equilibrium. Using a variety of simulation methods we have simulated their melting behavior and evaluated their propensity for thermal dissociation. The connection between equilibrium and dissociation properties, which has already been put forward in the experimental search for finite size phase transitions,^{37–40} is used here to assess the extent to which the branching ratio is sensitive to the ergodic hypothesis. By “enforcing” ergodicity through appropriate Monte Carlo sampling of the initial conditions, differences in the dissociation and relaxation time scales can be appreciated on this primary dissociation observable. The present findings confirm the strong relation between equilibrium and fragmentation statistics, and indicate how the latter can be used as an indirect probe of ergodicity (or lack thereof) with possible experimental relevance.

The article is organized as follows. In Sec. II, we describe the systems under investigation and, briefly, the various computational methods used to simulate them in the equilibrium and dissociating regimes. The results are presented and discussed in Sec. III, before some concluding remarks close the paper in Sec. IV.

II. METHODS

Most of the present work relies on Monte Carlo and molecular dynamics simulations for the thermodynamical and kinetic aspects, respectively. Those simulations require some knowledge of the global minimum structures in order to address their properties across a broad range of internal energy or temperature.

A. Binary Morse clusters

We consider clusters $A_N B_M$ of $N = M = 50$ particles bound by the Morse potential,

$$V(r) = D e^{\rho(r_0 - r)} (e^{\rho(r_0 - r)} - 2), \quad (1)$$

where D is the well depth, r_0 is the equilibrium distance, and ρ is the range. Following previous works^{34,35} we set both D and r_0 to unity for all A-A, A-B, and B-B interactions, and a simple combination rule $\rho_{AB} = (\rho_A + \rho_B)/2$ for the range of the mixed interaction, given the ranges ρ_A and ρ_B of the two

alike pairs. The clusters are thus characterized by the pair of ranges, denoted as $[\rho_A; \rho_B]$ with $\rho_A < \rho_B$, and chosen from the three series $[\rho; 12 - \rho]$ and $[\rho; 6]$ with $\rho = 3, 3.5, 4, 4.5, 5, 5.5, 5.7, 5.9$, as well as $[6; \rho]$ with $\rho = 6.1, 6.3, 6.5, 7, 7.5, 8, 8.5, 9$. Relative to the LJ interaction that is equivalent to $\rho = 6$ and considered to be medium ranged, ranges lower (higher) than 6 will be denoted as long (short). Additional pairs of long ranges $[\rho_A < 6; \rho_B < 6]$ will also be occasionally considered for the purpose of the discussion.

In the present work, we have determined the melting properties of the clusters $A_N B_N$ and their propensity to evaporate particles as a function of internal energy. In order to support the molecular dynamics simulations with a statistical analysis based on the Weisskopf theory⁴¹ (vide infra), the microcanonical densities of states must be evaluated also for the dissociation products $A_{N-1} B_N$ and $A_N B_{N-1}$.

The first task consisted of locating the global minimum (GM) structures for the parent and evaporation products, from which the simulations could be subsequently carried out. Basin-hopping global optimization⁴² with particle exchange moves was performed to produce low-energy structures from which the putative global minima are to be found. The structures collected at this stage generally fall into two groups, depending on whether short- or long-range interactions dominate bonding. Some global minima are depicted in Fig. 1 for the four specific systems $[3;9]$, $[3;6]$, $[6;9]$, and $[5.9;6.1]$. While the two former clusters with long-range interactions $[3;9]$ and $[3;6]$ are essentially polytetrahedral and roughly spherical, the two clusters $[6;9]$ and $[5.9;6.1]$ with medium- or long-range interactions only are close-packed with clear (111) facets. Those results are consistent with the seminal work by Doye and co-workers,¹⁴ and confirm the role of the range on

FIG. 1. Putative global minima of $A_{50}B_{50}$ binary Morse clusters with selected pairs $[\rho_A; \rho_B]$ of ranges.

structural order. As far as chemical order is now concerned, all clusters exhibit a clear core/shell phase separation, consistently with our previous analysis.³⁵ At the present size and composition, there are not enough B particles to coat the core of A particles completely, and several long-range particles are on the outside. The detailed chemical order is rather sensitive to the range, as illustrated by the two clusters with medium or short-range interactions [6;9] and [5.9;6.1], which share a common close-packed structure but slightly differ in the most stable homotop.⁴³

The cases illustrated here are representative of the vast majority of all binary Morse clusters considered in this work, with a distinct trend to exhibit polytetrahedral structures as soon as long-range interactions are present, close-packing being observed only when all interactions are medium- or short-ranged.

B. Finite temperature properties

Parallel tempering Monte Carlo^{5,6} simulations were performed to sample the configuration space of binary Morse clusters at thermal equilibrium. In addition to particle displacement and swaps between adjacent trajectories, exchanges between unlike particles were attempted to accelerate the sampling of homotops. In the context of thermal equilibrium, it is important not to allow any dissociation of the system,⁴⁴ and this was ensured by enclosing the clusters into a hard-wall spherical container with a radius of 5 units around the cluster center of mass. As shown by Moseler and Nordiek,²⁰ this introduces some minor dependence of the thermodynamical properties on the container radius at high temperatures, especially in the case of short-range interactions where the density of the fluid phase is most affected. Other methods can be used to constrain the sampling to connected clusters in Monte Carlo, for instance using a Stillinger criterion,^{24,45} but they are more involved and would need tuning for binary clusters.

Two types of exchange Monte Carlo simulations were carried out, in the canonical and microcanonical⁴⁶ ensembles. While canonical simulations are easier to interpret and discuss as a function of the temperature parameter, simulations at fixed total energy are more appropriate to connect with the simulations of dissociation, in which the control parameter is microcanonical. From those simulations, several properties were considered in order to interpret the melting mechanisms. Here we focus on the canonical heat capacity $C_v(T)$, which provides a natural connection with phase changes, and on a dedicated structural order parameter $\chi = R_{g,A}^2/R_{g,B}^2$ based on the gyration radii $R_{g,X}$ specific to $X=A$ or B particles. This quantity is suitable to probe changes in the core/shell arrangement in the cluster, notably alloying transitions or melting of the outer layer. The two aforementioned properties were obtained as a continuous function of temperature using the weighted histogram analysis method,⁴⁷ which incidentally also provides the configurational densities of states $\Omega_c(V)$ as a function of potential energy V . From Ω_c , the complete vibrational DOS $\Omega(E)$ can be obtained by simple convolution with the exact kinetic DOS, $\Omega_k(K) \propto K^{v/2-1}$, $v = 3(N + M) - 6$ being the number of independent degrees

of freedom.⁴⁴ In turn, the densities of states are related to microcanonical properties, starting with the temperature $T_\mu(E)$ such that $(k_B T_\mu)^{-1} = (\partial \ln \Omega / \partial E)$. This quantity will be discussed in relation with the variations of the dissociation rates.

In addition, we performed quenching analyses of the Monte Carlo trajectories, locally optimizing 1000 configurations into their so-called inherent structures (IS). Those minima provide a direct connection with the energy landscape, and can be used to represent the free-energy equilibrium phase. The Monte Carlo simulations covered the reduced temperature range of $0.05 \leq T \leq 0.5$, with 32 temperatures allocated according to a geometric progression in this range. Each simulation consisted of 10^8 Monte Carlo sweeps per temperature, following as many sweeps discarded for equilibration. Exchange Monte Carlo simulations in the microcanonical ensemble were performed at the same total energies as the molecular dynamics simulations of dissociation as described below. The exchange Monte Carlo simulations with swapping moves are much more efficient than conventional molecular dynamics in sampling configuration space, especially in the miscible regime. We then assume that the distribution of inherent structures produced from the MC simulations faithfully represent ergodic samples, and that initiating the dissociating MD trajectories from those distributions is a practical way of achieving global ergodicity.

C. Statistical dissociation

The stability against evaporation at finite temperature depends critically on the range.^{13,20} To address this issue and get quantitative insight into the dissociation kinetics of binary Morse clusters, we first performed series of molecular dynamics simulations at increasing values of the total energy E . The statistics of clusters having emitted an A or B particle, with numbers, respectively, denoted as $\mathcal{N}_A(t)$ and $\mathcal{N}_B(t)$, are accumulated as a function of time after thermal excitation. Assuming simple first-order kinetics, the total number $\mathcal{N}(t)$ of clusters having survived evaporation at time t is such that

$$\mathcal{N}(t) = \mathcal{N}_0 \exp[-(k_A + k_B)t], \quad (2)$$

where $\mathcal{N}_0 = \mathcal{N}(0)$ is the total number of trajectories, k_A and k_B are the dissociation rate constants corresponding to channels A and B, respectively. Similarly $\mathcal{N}_X$, $X=A$ or B is expressed as

$$\mathcal{N}_X(t) = \frac{k_X \mathcal{N}_0}{k_A + k_B} \{1 - \exp[-(k_A + k_B)t]\}. \quad (3)$$

In the absence of other channels, the branching ratio $\xi = \mathcal{N}_A/\mathcal{N}_B$ is thus a constant also equal to the ratio k_A/k_B between the rates. While the global dissociation rate $k_A + k_B$ can be obtained from the logarithmic variations of $\mathcal{N}(t)$, the individual rates k_X cannot. Instead, they can be related to the linear variations of $\mathcal{N}_X$ in the limit of short times, which gives $\mathcal{N}_X \approx \mathcal{N}_0 k_X t$. This approximation obviously requires that a sufficient number of dissociation events occur over short times, which in turn indicates that a sufficient energy must be reached given the duration of the trajectory.

The computational procedure to simulate the system and detect its evaporation is inspired from Weerasinghe and

Amar,⁹ and consists of thermalizing the system at a low total energy E_{eq} only as a mean of equilibrating it prior to the thermal excitation. This first stage of the MD trajectory is carried out under the constraints of vanishing linear and angular momenta. After a short period t_{eq} , the configuration is suddenly heated by scaling all velocities in order that the total energy of the system reaches the target value E . The trajectory is said to have evaporated if a particle exceeds a distance $R_{\text{diss}} = 15$ units from the center of mass. The evaporation time is then recorded as the last time this particle had a negative radial velocity.⁹

One difficulty with molecular dynamics simulations of evaporation is their poor efficiency at low energies, due to increasingly long times needed to observe dissociation events. A useful alternative technique lies in statistical rate theories, which can be quantitative provided that anharmonicities are accounted for.^{9,11} Here we use the Weisskopf approach from nuclear physics,⁴¹ which is of comparable accuracy as phase space theory for non-rotating systems.¹⁰ According to this theory, the dissociation rate k_X corresponding to the emission of X particles can be cast as^{10,41}

$$k_X(E) = \gamma_X \frac{\int_0^{E-\Delta_X} \varepsilon \Omega_X(E - \Delta_X - \varepsilon) d\varepsilon}{\Omega(E)}, \quad (4)$$

where Δ_X is the dissociation energy, or the energy difference between the most stable structures of the parent and product, ε denotes the kinetic energy released in the dissociation process, Ω and Ω_X the microcanonical densities of states of the

parent and product, respectively. In the above equation, γ_X is a prefactor containing various physical constants and symmetry factors.^{9,41} All energetic ingredients are known from the global minima, and the densities of states are a byproduct of the Monte Carlo simulations through the use of histogram reweighting. Thus, only γ_X remains unknown, and instead of predicting it from first principles we adopt a more pragmatic strategy by calibrating its value from a reference rate k_X obtained at a sufficiently high reference energy suitable for MD trajectories. This hybrid statistico-dynamical approach has been successfully used in the past^{9,10} as a way to correct for the poor knowledge of some ingredients of γ_X .

All molecular dynamics simulations used a time step of 10^{-2} reduced units, and individual trajectories were propagated for a maximum of 10^5 time steps, unless one evaporation event occurred earlier. 10^4 independent trajectories were propagated for each total energy E considered, and they were initiated either from the global minimum or from an equilibrated sample of inherent structures gathered at the very same energy from microcanonical Monte Carlo simulations.

III. RESULTS AND DISCUSSION

As was the case for the stable structures, we discuss the thermodynamical properties of only a representative subset of clusters for which the global minima are depicted in Fig. 1. The variations of the heat capacity and the variance of the ratio of gyration radii χ with canonical temperature are depicted in Fig. 2. The heat capacities generally exhibit one main

FIG. 2. Heat capacities (black curves) and fluctuations of the ratio $\chi = R_{g,A}^2/R_{g,B}^2$ of gyration radii between A and B elements (red curves), for $A_{50}B_{50}$ clusters with selected pairs $[\rho_A;\rho_B]$ of ranges and as a function of canonical temperature T . (a) $[\rho_A = 3;\rho_B = 9]$; (b) $[\rho_A = 3;\rho_B = 6]$; (c) $[\rho_A = 6;\rho_B = 9]$; (d) $[\rho_A = 5.9;\rho_B = 6.1]$.

FIG. 3. Distributions of inherent structures obtained from local minimization of configurations sampled in the Monte Carlo simulations at various temperatures T , for $A_{50}B_{50}$ binary Morse clusters with selected pairs $[\rho_A; \rho_B]$ of ranges. For each cluster, representative structures are depicted. (a) $[\rho_A = 3; \rho_B = 9]$; (b) $[\rho_A = 3; \rho_B = 6]$; (c) $[\rho_A = 6; \rho_B = 9]$; (d) $[\rho_A = 5.9; \rho_B = 6.1]$.

melting peak as well as an additional peak or shoulder either on the low temperature side (case of $[5.9; 6.1]$) or at higher temperatures (other cases). As will be seen below, these complex features have a counterpart in the microcanonical ensemble, where the temperature varies non-monotonically with increasing total energy.

The two clusters with long-range interactions undergo two changes in their phase separated structure, the increase in the fluctuations of χ near $T = 0.21$ being associated with the melting of the B-rich outer layer. As temperature increases further the A-rich core becomes more and more fluxional and eventually melts with a clear thermal signature near $T = 0.3$ for $[3; 9]$, although this feature is absent in the other system $[3; 6]$.

In contrast, the two clusters with medium- or short-range interactions only show a dominating dramatic event for χ near $T = 0.29$, associated with a sharp peak in the heat capacity and followed by a decrease in χ at higher temperatures. The decrease of χ for $0.1 \leq T \leq 0.22$ in the case of the $[5.9; 6.1]$ system indicates that this quantity must reach a maximum below $T = 0.1$, because it is expected to vanish at $T = 0$. For these two clusters, the heat capacities actually show rather similar variations, with two asymmetric shoulders on both sides of the main peak and possibly turning into a bump in the $[6; 9]$ case. Those features reflect the complex interplay between structural and chemical order in those binary clusters.

More insight is provided by considering the inherent structures visited during the simulations. Anticipating that the molecular dynamics simulations will be conducted at constant

energy and possibly starting from a pool of equilibrated structures, we show in Fig. 3 various energy distributions obtained from microcanonical exchange Monte Carlo trajectories at different total reduced energies E , for the same four clusters discussed so far. In order to make them comparable across the various systems, those energies are expressed in reduced form relative to the global minimum energy and normalized by the number ν of degrees of freedom. Hence they span the same typical range as temperatures. For each system, three energies have been selected roughly below and above the melting point. The energy gap ΔE between the low- and high-energy distributions reflects the latent heat of melting, and occasionally (for $[3; 6]$ and $[5.9; 6.1]$ at $\Delta E = 20$) some energies happen to lie near coexistence regions with dual peaks both at low and high energies. The energy gap is particularly large for the clusters bound by short-range interactions, about twice as for the clusters having long-range interactions. Inspecting the inherent structures reveals that the core/shell phase separation pattern is preserved in the latter systems, even in the liquid. Already at the lowest energy considered do the shape of the clusters fluctuate between many isomers differing mostly in the arrangement of the outer layer of B particles. The A core is indirectly affected, but increasingly softens and eventually melts through occupying many more isomers.

Clusters bound at medium or short range only undergo a completely different melting process, as they first mix while keeping their close-packed structural order. This process is reminiscent of the alloying transition in some metals such as Pd-Pt³⁶ or Ag-Au,⁴⁸ and shows that entropic effects are

crucial at finite temperature, energetics alone being insufficient to explain the great diversity of inherent structures obtained at low total energy, mostly based on very few structural isomers. The absence of homotops in the case of clusters with long-range interactions can be explained by the greater cost of substituting defects by A-B permutations, A particles being more reluctant to occupy surface sites. However, it is important to notice that not only do the [3;9] and [3;6] clusters have some long-range interactions, but there is a significant mismatch between alike and unlike interactions that is absent in the [5.9;6.1] case. Therefore, the tendency to mix is not a mere consequence of the stable structures being close-packed, it also requires a sufficiently small mismatch between interactions. This mismatch is more consequential in the case of long-range interactions because when $\rho > 6$ the particles are less sensitive to the environment beyond nearest neighbors. Thus we expect clusters bound only at long ranges such as $[x;y]$ with $x < y < 5$ to be polytetrahedral but still prone to mixing, at least in the limit $y \rightarrow x$, and more generally the normalized range mismatch $(y - x)/(y + x)$ to be a determining factor of structural trends at finite temperature (phase separation occurring at zero temperature at any finite range mismatch).

Based on the above simulation results, the role of range and range mismatch on the equilibrium thermodynamics appears more clearly. The interplay between structural and chemical order gives rise to a premelting phase in which B particles are either disordered around a rigid A core (long-range interactions) or mixed with it (medium or short-range interactions only). As we will now see, these two radically different phases influence the dissociation pattern in a non-trivial way, to the extent that evaporation could be used as a probe of equilibration and ergodicity.

We show in Fig. 4, the number of trajectories of the cluster with ranges [6;9] and total reduced energy $E = 0.4$ hav-

FIG. 4. Number of molecular dynamics trajectories of the $A_{50}B_{50}$ cluster with $\rho_A = 6$ and $\rho_B = 9$ having dissociated a A particle (black symbols) or a B particle (red symbols) after a thermal excitation at total reduced energy of $E = 0.4$ and as a function of time. The trajectories are initiated either from the global minimum (empty symbols) or randomly drawn from the equilibrium distribution of inherent structures at this energy (full symbols). In all cases, the linear variations at short times are highlighted by the corresponding slopes.

ing emitted a A or B particle as a function of time. In a first set of simulations, the trajectories were all initialized from the global minimum structure. In a second set, each trajectory was initialized from a random inherent structure gathered from a microcanonical exchange Monte Carlo trajectory at the corresponding total energy. This protocol mimics thermal equilibration and ignores the kinetics and the time needed to reach this equilibrated phase. For both types of preparations, the populations $N_X(t)$ follow the kinetics expressed by Eq. (3), and the dissociation rates obtained from the slopes at $t \rightarrow 0$ are much higher for B particles, as expected from their lesser stability and preference for outer locations. From Fig. 4, the branching ratio ξ between channels A and B can be obtained from the definition as the ratio of populations, leading to $N_A/N_B = 0.0150$ or 0.0955 for trajectories initiated either from the global minimum or from the equilibrated sample, respectively. Alternatively, the branching ratios can be evaluated from the rate constants, respectively, as $k_A/k_B = 0.0155$ and 0.0958 , in good agreement with the two previous numbers.

This example shows that the dissociation kinetics may depend quite sensitively on the initial conditions. In the case of the [6;9] cluster, inspection of Fig. 3(c) indicates that the equilibrium phase at $E = 0.4$ is both structurally and chemically melted. Systems bound by long-range interactions and without mixing tendencies do not exhibit such a strong difference in the branching ratio depending in whether the trajectories are initialized from the global minimum or from equilibrated samples. Therefore, the discrepancies between the results obtained from the two simulation protocols are directly related to the occurrence of the alloying premelting transition.

Those results are of course not specific to the [6;9] cluster, and similar observations can be made for clusters with a mixing tendency. Fig. 5 shows for instance the probability $p_A = \xi/(1 + \xi)$ that A particles dissociate first for the series $[\rho; 12 - \rho]$ with $\rho = 5, 5.5, 5.7$, and 5.9 , as obtained from the two simulation protocols and as a function of reduced

FIG. 5. Probability of emitting a particle A upon thermal dissociation of $A_{50}B_{50}$ binary Morse clusters with pairs of ranges $[\rho_A = \rho; \rho_B = 12 - \rho]$, for $\rho = 5, 5.5, 5.7$, and 5.9 , as obtained from molecular dynamics trajectories initiated either from the global minimum (empty symbols) or randomly drawn from equilibrium distributions of inherent structures (full symbols), as a function of reduced internal energy E .

internal energy in the range $E = 0.3$ – 0.6 . The probability of preferentially emitting A particles generally increases with ρ , which is the expected trend and only expresses that the two types of particles become less distinguishable as $\rho \rightarrow 6$. Simulations starting from the core/shell global minimum exhibit rather strong energy-dependent variations of p_A with internal energy, and a broad maximum near $E \sim 0.5$. In contrast, simulations starting from equilibrated samples show much weaker and steady variations except at low energy with some apparent non-monotonic fluctuations. In all cases, equilibration of the initial conditions leads to higher probabilities p_A , and the discrepancies increase as ρ tends to 6 with respect to the perfectly mixed asymptotic limit $p_A = 1/2$. Such differences are also found for the other series of binary Morse clusters $[6;\rho]$ with $\rho > 6$ and $[\rho;6]$ with $\rho < 6$, especially as $\rho \rightarrow 6$. In highly non-miscible systems with long-range interactions and a sufficient range mismatch, both types of simulations lead to vanishingly small probabilities p_A and cannot be told apart.

The discrepancies in the apparent kinetics of dissociation when changing the cluster initial state point to some key role played by equilibration or ergodicity and the specific time scale associated with global relaxation. To further clarify this issue, we have used the Weisskopf theory to provide quantitative predictions of the dissociation kinetics over broad energy ranges. Essential for this approach is that, in principle, it describes thermal dissociation as a fully equilibrium property. In the present work, this connection is made through the densities of states of the parent and product clusters, which rely on the use of ergodic samples provided by exchange Monte Carlo simulations. Comparing the raw MD results to the predictions of the Weisskopf theory is another way to assess the role of equilibration on the dissociation observables.

The rate constants evaluated from the short time variations of the populations have been represented in Fig. 6 as a function of total energy E (in reduced units), for the typical

FIG. 6. Evaporation rate constants k_A and k_B from the $A_{50}B_{50}$ cluster with ranges $[6;7]$ as a function of reduced internal energy. The results are obtained from molecular dynamics simulations initiated either from equilibrium samples of inherent structures or from the global minimum (full and empty symbols, respectively), and from the Weisskopf rate theory with anharmonic densities of states (thick solid lines). The inset emphasizes the variations of the microcanonical temperature of the parent and evaporation products $A_{49}B_{50}$ and $A_{50}B_{49}$ near the melting region.

example of the $[6;7]$ cluster. Again, the rates obtained from the two simulation protocols appear rather different, the trajectories initiated from the global minimum always producing an excess (lack) of A (B) dissociated particles relative to trajectories initiated from equilibrated samples. Interestingly, the variations of the rates with internal energy always exhibit at least one convex region, and even two for equilibrated initial conditions. To interpret those complex variations, we have calibrated the predictions of the Weisskopf theory on the values of the rates at $E = 0.4$, adjusting the prefactors γ_X accordingly. The Weisskopf rates quantitatively reproduce the variations of the MD data obtained from the equilibrated initial conditions, and notably also show the two convex regions that are not present in the other set of MD data. The agreement between the equilibrated MD data and the predictions of the Weisskopf theory confirms the validity of the latter, and shows the accuracies of the densities of states obtained from the exchange Monte Carlo simulations.

We now wish to interpret the occurrence of two convex regions in the variations of the rate constants, an unusual observation, whereas single convex parts have already been reported^{9,10} and interpreted as signatures of phase transitions. We first notice that the Weisskopf expression of Eq. (4) involves two densities of states (for the parent and dissociation product), hence a single convex part in each quantity could be sufficient to yield two convex regions in the resulting rate. However, all three densities of states turn out to have more than one convex part, as illustrated by the microcanonical temperature T_μ whose variations are depicted as an inset in Fig. 6. For the parent $A_N B_N$ and the two products $A_{N-1} B_N$ and $A_N B_{N-1}$, the two backbendings in the microcanonical temperature are equivalent to two convex regions in the densities of states,⁴⁴ and are a microcanonical manifestation of the pre-melting features in the canonical heat capacities. At this stage, the two convex regions in the rate constants could originate from any combination involving the parent and product. Yet we notice that these regions occur at the same energy as their counterpart in the parent temperature ($E \simeq 0.35$ and 0.43), and it is likely that the convolution in the numerator of Eq. (4) smears out such details. Based on those arguments, we attribute the two convex regions in the variations of the rate constants to the thermodynamical properties of the parent rather than the dissociation products.

The similarity between the predictions of the Weisskopf theory and the MD trajectories initiated from the equilibrated samples is consistent with the equilibrium nature of the Monte Carlo simulations used to extract the densities of states. The discrepancies with the alternative set of MD trajectories initiated from the global minimum are then indicative that those latter simulations did not behave ergodically, and more precisely than they dissociated before reaching equilibrium. This conclusion is confirmed by comparing now the MD results to the Weisskopf predictions for the probability p_A , which are shown in Figs. 7–9 for the cluster series $[\rho;12 - \rho]$, $[6;\rho]$, and $[\rho;6]$, respectively. Here only the MD results from equilibrated samples are shown, and the Weisskopf predictions have been again calibrated from the data at reduced energy $E = 0.4$. In the cases with long-range interactions (Figs. 7 and 9), only the systems that have a modest range mismatch,

FIG. 7. Probability of emitting a particle A upon thermal dissociation of $A_{50}B_{50}$ binary Morse clusters with pairs of ranges $[\rho_A = \rho; \rho_B = 12 - \rho]$, for $\rho = 5, 5.5, 5.7$, and 5.9 , as obtained from molecular dynamics trajectories initiated from equilibrium distributions of inherent structures (symbols), and predicted from the statistical rate theory (full curves), as a function of reduced internal energy E .

and a substantially high probability p_A , are illustrated. The agreement between the MD results and the predictions of the statistical theory is good in general, at least as far as trends are concerned. This is not completely fortuitous, because both approaches fundamentally incorporate thermal equilibrium in their assumptions as well as constructions, densities of states and initial conditions being all drawn from exchange Monte Carlo simulations. The continuous curves resulting from the Weisskopf approach often show bumps and non-monotonic features, especially at moderate energies where MD simulations of evaporation are barely feasible. Despite the greater difficulty of accumulating statistics in this regime, we believe that those features are genuine, because they systematically arise for various pairs of ranges. Yet, since in the Weisskopf approach they originate from the complex variations of den-

FIG. 8. Probability of emitting a particle A upon thermal dissociation of $A_{50}B_{50}$ binary Morse clusters with pairs of ranges $[\rho_A = 6; \rho_B = \rho]$, for $\rho = 6.1, 6.5, 7.5$, and 9 , as obtained from molecular dynamics trajectories initiated from equilibrium distributions of inherent structures (symbols), and predicted from the statistical rate theory (full curves), as a function of reduced internal energy E .

FIG. 9. Probability of emitting a particle A upon thermal dissociation of $A_{50}B_{50}$ binary Morse clusters with pairs of ranges $[\rho_A = \rho; \rho_B = 6]$, for $\rho = 4.5, 5, 5.5$, and 5.9 , as obtained from molecular dynamics trajectories initiated from equilibrium distributions of inherent structures (symbols), and predicted from the statistical rate theory (full curves), as a function of reduced internal energy E .

sities of states spanning many orders of magnitude, the quantitative accuracies are difficult to assess. Comparing Figs. 5 and 7 for the $[\rho; 12 - \rho]$ clusters series, the predictions of the statistical rate theory are only compatible with the MD data obtained assuming equilibrated initial conditions. The same level of agreement holds for the other series, the results being omitted for the sake of brevity.

Focusing now on the interpretation of those results, we first notice that clusters undergoing an alloying transition at low temperature will expose A particles much more likely than in their core/shell phase separated ground state. In itself, this simply explains why starting from a mixed structure necessarily increases the likeliness of emitting a A particle. However, invoking purely thermodynamics is not sufficient, because clearly the kinetics of isomerization is at play as well when discussing stability against dissociation. By simulating the thermally equilibrated phase by means of a Monte Carlo approach, such kinetic issues were actually bypassed. In contrast, the cluster initially placed in its global minimum structure requires some time to statistically relax to its free energy equilibrium phase, and the competition between this relaxation time and the time for dissociation is the key to the difference in the branching ratios observed in the two types of MD simulations. As shown notably in the case of metallic alloys,³³ but as also known in the case of rare-gas clusters,² the atomistic mechanisms producing the alloyed phase involve many rearrangements and significant energy barriers that are comparable with the dissociation energies themselves. Here, clusters with a strong mixing tendency are also those with shorter range interactions, for which sublimation prevails over melting. Those two factors combine to destabilize B particles more than in the equilibrated cluster.

The picture emerging from these selected examples can be extrapolated to predict the trends for other clusters. For instance, systems bound at long range but nevertheless with mixing tendencies should be expected if the two ranges are below 6 but with a small mismatch. In this case, the

FIG. 10. Probability of emitting a particle A upon thermal dissociation of $A_{50}B_{50}$ binary Morse clusters with long-range interactions [4;4.1], [4;4.5], and [5;5.1], as obtained from molecular dynamics trajectories initiated from the global minimum (open symbols connected by dashed lines), from structures drawn from equilibrium distributions of inherent structures (full symbols), and predicted from the statistical rate theory (full curves), as a function of reduced internal energy E .

clusters should chemically mix before they melt. However, because of the long-range interactions the liquid state should become much more stable, evaporation being slower. We thus anticipate that the branching ratios should not depend so critically on the initial conditions, the presence of long-range interactions being here the dominant factor over a small range mismatch. In order to verify these speculations, we have performed additional simulations for the [4;4.1], [4;4.5], and [5;5.1] systems. The global minima of the [4;4.1] and [5;5.1] clusters, as depicted in Fig. 10, respectively, show polytetrahedral and close-packed shapes, indicating that the latter system should actually be classified as medium-ranged. The probabilities of emitting preferentially A particles are shown in the same figure as a function of internal energy, the initial configurations of the MD trajectories being either drawn from the distribution of inherent structures or kept fixed as the global minimum. For the three clusters, the predictions of the Weisskopf theory have also been estimated from the corresponding densities of states and calibrated from the (equilibrated) MD statistics at $E = 0.5$. Those predictions are again fairly similar to the overall variations of the MD data in the entire energy range considered, notably they still show some significant non-monotonic parts. Initiating the MD trajectories from the global minimum no longer affects the dissociation statistics to a large extent, even though interactions are long ranged. This confirms our interpretation that the mixing character, induced here by the proximity of the interactions between unlike particles, cannot explain by itself the lack of ergodicity manifested in the dissociation statistics.

The relative influences of range and range mismatch on the propensity for emitting particles of either type can further be discussed by considering the branching ratio at fixed temperature. Assuming equilibrated initial conditions, the variations of the probability p_A with range are represented in Fig. 11(a) for the three range series $[\rho; 12 - \rho]$, $[6; \rho]$, and $[\rho; 6]$ and at the two reduced internal energies $E = 0.3$ and 0.5 .

FIG. 11. Probability of emitting a particle A upon thermal dissociation of $A_{50}B_{50}$ binary Morse clusters at the two reduced internal energies $E = 0.3$ and 0.5 , for various pairs of ranges $[\rho_A; \rho_B]$ and from initial conditions (a) taken from equilibrated samples or (b) fixed at the global minimum.

As expected, the probability smoothly converges to $1/2$ as $\rho \rightarrow 6$ in the three cases, and increases with decreasing range mismatch $|\rho_B - \rho_A|$. The results of Fig. 11 are also not symmetric around $\rho = 6$, emphasizing that the range mismatch has a much greater effect at long range, different short-range interactions having a mixing tendency anyway. Increasing the internal energy from $E = 0.3$ to 0.5 obviously increases the overall dissociation probability, but at the expense of B particles. This is a nontrivial result, which actually conveys that temperature favors chemical disorder. Initiating now the MD simulations from the global minimum, the effects of the range on the probability are shown in Fig. 11(b). They are particularly drastic at the low excitation energy $E = 0.3$, where equilibration appears to have clearly failed, without seemingly converging to $p_A = 1/2$ in the complete mixing limit $\rho = 6$. However, this behavior is recovered at $E = 0.5$, becoming more comparable, though still underestimated, with respect to the equilibrated reference results. Those effects are consistent with the faster isomerization rate expected at higher temperature, and again highlight the competition between global relaxation and evaporation in those clusters.

The contrast between the MD results obtained under different assumptions regarding their initial conditions is thus a manifestation of very different isomerization and dissociation kinetics. This emphasizes the possibility of detecting from the branching ratio whether a mixed system produced in statistical amounts has behaved ergodically by reaching equilibrium or if it has remained in a metastable state. Some nanoscale metallic systems that exhibit alloying transitions^{36,48} could act as experimental candidates of our theoretical findings,

provided that they do not have a highly stable liquid phase (consistent with the long range of their interactions) preventing them from evaporating particles until they are fully disordered. Mesoscopic clusters of colloidal particles, as recently synthesized in the Manoharan group,⁴⁹ would be much more suitable for experimental verification. Binary clusters of such particles could be generated from spheres with different radii, and owing to the very short range of the interactions those clusters should exhibit a strong mixing propensity. Observing signatures of non-equilibrium behavior in those clusters would pose a number of challenges, starting with the need to characterize the equilibrium phases. Binary clusters with short-range interactions should have a huge number of stable minima and homotops,¹⁷ hence this probably would impose upper limits on the number of particles. Additionally, reaching equilibrium would imply a large set of independent realizations, but would also require dedicated relaxation schemes to ensure equilibrium was reached. Perhaps a physical container similar to the one used in the present Monte Carlo simulations, with an appropriate shaking procedure, could achieve this goal.

Alternatively, experiments on atomic clusters could be attempted if long observation times can be accessed, as with trapping devices or storage rings. With appropriate detection, such experiments could probe the dissociation statistics as a function of time after excitation, from which the rates and, more importantly, the branching ratio could be evaluated. Any significant drift of this ratio over time would reveal a change in the underlying occupation of configurational space, and be used as a possible probe of non-ergodicity. Suitable candidates to test those ideas could be mixed krypton-xenon clusters, whose mixing tendency³⁵ could be preserved upon ionization, as needed in such experiments.

IV. CONCLUDING REMARKS

Owing to the difficulty of characterizing the full equilibrium state, manifestations of non-ergodic behavior in complex systems are seldom prone to direct and conclusive evidence. With their rich structural and thermal phenomenology, binary Morse clusters provide a valuable class of systems exhibiting various types of chemical ordering, possible structural transitions, and a strong dependence of their dissociation propensity on the range of the interaction. The time scales associated with structural and chemical relaxation can be evaluated against the fragmentation time scale by comparing dissociation properties obtained from suitably prepared initial conditions. This strategy relies on a robust method for enforcing equilibrium sampling, chosen here as microcanonical exchange Monte Carlo combined with local minimizations.

By varying the ranges and their mismatch, our simulations have shed light onto various possible behaviors at and out of thermal equilibrium. The global minima follow the same phenomenology as was found in homoatomic clusters,¹⁴ with close packed structures at short range and polytetrahedral shapes at long range, but the core/shell phase separation pattern is found for all combinations of ranges. At finite temperature, clusters partially bound at long range keep their phases separated until the outer particles melt and evaporate.

In contrast, when short-range interactions dominate the clusters exhibit an alloying transition before they melt. The complex interplay between structural and chemical order gives rise to multiple features in the canonical and microcanonical caloric curves.

The resistance to thermal evaporation was considered by direct molecular dynamics simulations assisted by a statistical analysis based on the Weisskopf theory, which practically assumes ergodicity to be fulfilled through the use of equilibrium densities of states. Miscible clusters bound at short range tend to emit an excess of short-range particles if they are excited directly from the global minimum, thereby indicating that evaporation occurred away from equilibration and that ergodicity cannot be attained because dissociation is too fast. If the miscible clusters are bound by long-range forces, the relaxation and dissociation times both increase and become closer to each other, ergodicity is restored.

Our analysis was partly based on the use of the Weisskopf rate theory and the known connection between dissociation and statistical equilibrium properties.^{8,9} By highlighting cases where the predictions of the rate theory deviate significantly from the MD results, the present results could be interpreted as the consequence of the incapability of the system to reach equilibrium. They also offer a means of detecting broken ergodicity in practical systems by looking at the branching ratio, suggesting some possible experimental confirmation, e.g., on mesoscopic clusters of colloidal spheres.⁴⁹

Tracking broken ergodicity in the dissociation behavior of homoatomic clusters would also be possible, at least in principle, if they exhibit well-defined structural transitions at low temperature such as in the case of the archetypal LJ₃₈ cluster.^{23,46} However, the fragmentation observables available for a homoatomic cluster are essentially limited to the rate constant and the kinetic energy released, and they may not be sensitive enough to the low-energy perturbations caused by the structural transitions.

Although the present computations were limited to a single cluster size, and putting aside specific finite size effects, the conclusions reached here about the roles of ranges and their mismatch on the finite temperature stability should be generally valid for arbitrary binary clusters. As a natural extension of this work, one could target bulk phase diagrams in two or three dimensions, and notably assess the combined roles of average range and mismatch on the nature and stability of the phase separated and mixed condensed phases as a function of composition. In the context of slow relaxation to thermal equilibrium, the question of glassy behavior could also be tackled, either from cooling simulations, or in a more detailed fashion by considering the general features of the energy landscape.² Obviously, the landscape perspective would be a natural extension useful to address the global relaxation kinetics also in clusters, as a complement to the more conventional simulations carried out so far.

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- ¹R. D. Mountain and D. Thirumalai, *Physica A* **210**, 453 (1994).
- ²D. J. Wales, *Energy Landscapes* (Cambridge University Press, Cambridge, 2003).
- ³B. A. Berg and T. Neuhaus, *Phys. Rev. Lett.* **68**, 9 (1992).
- ⁴F. Wang and D. P. Landau, *Phys. Rev. Lett.* **86**, 2050 (2001).
- ⁵R. H. Swendsen and J.-S. Wang, *Phys. Rev. Lett.* **57**, 2607 (1986).
- ⁶G. Geyer, in *Proceedings of the 23rd Symposium on the Interface in Computing Science and Statistics*, edited by E. K. Keramidas (Interface Foundation, Fairfax Station, NY, 1991), pp. 156.
- ⁷V. A. Sharapov, D. Meluzzi, and V. A. Mandelshtam, *Phys. Rev. Lett.* **98**, 105701 (2007).
- ⁸M. F. Jarrold, "Introduction to statistical reaction theories," in *Clusters of Atoms and Molecules I*, edited by H. Haberland (Springer, Berlin, 1991).
- ⁹S. Weerasinghe and F. G. Amar, *J. Chem. Phys.* **98**, 4967 (1993).
- ¹⁰F. Calvo and P. Parneix, *J. Chem. Phys.* **126**, 034309 (2007).
- ¹¹G. H. Peslherbe and W. L. Hase, *J. Phys. Chem. A* **104**, 10556 (2000).
- ¹²J. P. K. Doye and D. J. Wales, *Science* **271**, 484 (1996).
- ¹³F. Calvo, *J. Phys. Chem. B* **105**, 2183 (2001).
- ¹⁴J. P. K. Doye, D. J. Wales, and R. S. Berry, *J. Chem. Phys.* **103**, 4234 (1995).
- ¹⁵J. M. C. Marques, A. A. C. C. Pais, and P. E. Abreu, *J. Comput. Chem.* **33**, 442 (2012).
- ¹⁶P. A. Braier, R. S. Berry, and D. J. Wales, *J. Chem. Phys.* **93**, 8745 (1990).
- ¹⁷M. A. Miller, J. P. K. Doye, and D. J. Wales, *J. Chem. Phys.* **110**, 328 (1999).
- ¹⁸D. J. Wales, *ChemPhysChem* **11**, 2491 (2010).
- ¹⁹B. M. Smirnov, A. Yu. Strizhev, and R. S. Berry, *J. Chem. Phys.* **110**, 7412 (1999).
- ²⁰M. Moseler and J. Nordiek, *Phys. Rev. B* **60**, 11734 (1999).
- ²¹P. Shah, S. Roy, and C. Chakravarty, *J. Chem. Phys.* **118**, 10671 (2003).
- ²²D. T. Mainz and R. S. Berry, *Mol. Phys.* **88**, 709 (1996).
- ²³J. P. K. Doye and D. J. Wales, *Phys. Rev. Lett.* **80**, 1357 (1998).
- ²⁴F. Calvo, J. P. K. Doye, and D. J. Wales, *Nanoscale* **4**, 1085 (2012).
- ²⁵R. Ferrando, J. Jellinek, and R. L. Johnston, *Chem. Rev.* **108**, 845 (2008).
- ²⁶I. L. Garzón, X. P. Long, R. Kawai, and J. H. Weare, *Chem. Phys. Lett.* **158**, 525 (1989).
- ²⁷A. S. Clarke, R. Kapral, and G. N. Patey, *J. Chem. Phys.* **101**, 2432 (1994).
- ²⁸L. J. Munro, A. Tharrington, and K. J. Jordan, *Comput. Phys. Commun.* **145**, 1 (2002).
- ²⁹P. Parneix, Ph. Bréchnignac, and F. Calvo, *Chem. Phys. Lett.* **381**, 471 (2003).
- ³⁰F. Calvo and E. Yurtsever, *Phys. Rev. B* **70**, 045423 (2004).
- ³¹J. P. K. Doye and L. Meyer, *Phys. Rev. Lett.* **95**, 063401 (2005).
- ³²J. M. Dieterich and B. Hartke, *J. Comput. Chem.* **32**, 1377 (2011).
- ³³F. Calvo, A. Fortunelli, F. Negreiros, and D. J. Wales, *J. Chem. Phys.* **139**, 111102 (2013).
- ³⁴D. Parodi and R. Ferrando, *Phys. Lett. A* **367**, 215 (2007).
- ³⁵F. Calvo and E. Yurtsever, *Comput. Theor. Chem.* **1021**, 7 (2013).
- ³⁶F. Calvo, *Faraday Discuss.* **138**, 75 (2008).
- ³⁷M. Schmidt, R. Kusche, W. Kronmüller, B. von Issendorff, and H. Haberland, *Phys. Rev. Lett.* **79**, 99 (1997).
- ³⁸C. O. Dorso, V. C. Latora, and A. Bonasera, *Phys. Rev. C* **60**, 034606 (1999).
- ³⁹C. Bréchnignac, Ph. Cahuzac, B. Concina, J. Leygnier, B. Villard, P. Parneix, and Ph. Bréchnignac, *Chem. Phys. Lett.* **335**, 34 (2001).
- ⁴⁰F. Gobet, B. Farizon, M. Farizon, M. J. Gaillard, J.-P. Buchet, M. Carré, P. Scheier, and T. D. Märk, *Phys. Rev. Lett.* **89**, 183403 (2002).
- ⁴¹V. Weisskopf, *Phys. Rev.* **52**, 295 (1937).
- ⁴²D. J. Wales and J. P. K. Doye, *J. Phys. Chem. A* **101**, 5111 (1997).
- ⁴³J. Jellinek and E. B. Krissinel, *Chem. Phys. Lett.* **258**, 283 (1996).
- ⁴⁴P. Labastie and R. L. Whetten, *Phys. Rev. Lett.* **65**, 1567 (1990).
- ⁴⁵F. H. Stillinger, *J. Chem. Phys.* **38**, 1486 (1963).
- ⁴⁶F. Calvo, J. P. Neirótti, D. L. Freeman, and J. D. Doll, *J. Chem. Phys.* **112**, 10350 (2000).
- ⁴⁷S. Kumar, D. Bouzida, R. H. Swendsen, P. A. Kollman, and J. M. Rosenberg, *J. Comput. Chem.* **13**, 1011 (1992).
- ⁴⁸F. Calvo, E. Cottancin, and M. Broyer, *Phys. Rev. B* **77**, 121406(R) (2008).
- ⁴⁹G. Meng, N. Arkus, M. P. Brenner, and V. N. Manoharan, *Science* **327**, 560 (2010).