Many-body effects on the melting and dynamics of small clusters

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Using a potential recently proposed by Baskes [Phys. Rev. Lett. **83**, 2592 (1999)], we study the influence of the many-body interactions on the thermodynamics and chaotic dynamics of small atomic clusters. With standard molecular dynamics simulations as well as parallel tempering Monte Carlo, we calculate the complete heat capacity curves and the variations of the largest Lyapunov exponent with total energy. We observe that increasing the magnitude or decreasing the range of the many-body forces leads to an increase of chaos and a decrease in the melting temperature. Decreasing the range of the many-body interactions also results in a significantly lower latent heat of melting.

Clusters offer a very convenient tool for studying the static and dynamical behaviors of molecular systems having many degrees of freedom.¹ They are small enough so that they can handle extensive computations, yet they display some of the important characteristics of the bulk phase, including melting and freezing. An additional point of interest is the presence of unique phenomena such as magic numbers in the mass spectra, and, more generally, their unusual properties changing as the size varies only by very few atoms.²

Although still not observed experimentally, clusters often melt through the so-called dynamical coexistence phenomenon, resulting from the different freezing and melting temperatures T_f and T_m .^{3,4} In the temperature range $T_f < T < T_m$, the back and forth fluctuations between the solidlike and liquidlike phases has been shown to be the cause of a backbending portion of the caloric curve in the microcanonical ensemble. Since the last decade, the theoretical approaches to the thermodynamical study of clusters have focused on the relationship between thermal observables (the caloric curve, melting point, latent heat of melting) and the topography of the underlying potential-energy surface (or ‘energy landscape’). In particular, Doye and Wales have clearly shown a strong correlation between the very low melting points of some particular Lennard-Jones (LJ) clusters (such as LJ₃₈) and the existence of competing low-energy structures.⁵ As shown by Hinde and co-workers, the topography of the potential surface also affects the chaotic behavior of the dynamics to a large extent.⁶

The classical approaches to the bonding in atomic clusters generally employ an additive potential energy function E :

$$E = \sum_i V_i + \sum_{ij} V_{ij} + \sum_{ijk} V_{ijk} + \dots \quad (1)$$

The internal individual energies V_i represent a global geometrical factor, but they are not of chemical importance. Two-body, three-body, and higher-order terms determine the behavior of the system. As the higher order body interactions are included in the above summation, the computational re-

quirements go up as N^m where N is the number of particles and m the order of the many-body interactions. Up to now, only a few investigations have been performed with higher order terms (usually, the three-body Axilrod-Teller potential), even though it is known that there are a large number of phenomena in which these terms play an important role. An alternative way to incorporate many-body interactions is provided by the embedded-atom formalism.⁷⁻⁹ Recently, Baskes proposed a potential based on the embedded-atom method and extended the pairwise LJ potential into the many-body regime.¹⁰ The potential function introduced by Baskes has a very simple analytical form

$$E(\mathbf{R}) = \sum_i \left[F(\bar{\rho}_i) + \frac{1}{2} \sum_{j \neq i} \phi(r_{ij}) \right], \quad (2)$$

$$F(\bar{\rho}) = (AZ_0/2) \bar{\rho} [\ln \bar{\rho} - 1], \quad (3)$$

$$\phi(r) = (1/r^{12}) - (2/r^6) - (2/Z_0) F[\rho(r)], \quad (4)$$

$$\bar{\rho}_i = \frac{1}{Z_0} \sum_{j \neq i} \rho(r_{ij}), \quad (5)$$

$$\rho(r) = \exp[-\beta(r-1)], \quad (6)$$

where Z_0 is the number of nearest neighbors (taken as 12 for the fcc lattice), A is a parameter that controls the extent of the many-body interaction, and β describes the decay of the electron density.

Several authors have investigated the effect of some particular aspects of the potential on the structure, dynamics, or thermodynamics of clusters. A great deal of attention has been given to the potential range by Wales and co-workers¹¹⁻¹³ and by others.^{14,15} More recently, the influence of the softness of the repulsive core has also been discussed.¹⁶ The Baskes potential was shown to provide a wide range of properties making it suitable not only for noble gases, but also for metals. In particular, it predicts very different static (solid structure) and thermodynamic (melting

point) properties when its parameters A and β are varied.¹⁰ Therefore we can expect this potential to display a very rich phenomenology associated with cluster melting.

In this report we only study the general behaviors of two clusters, and particularly the variations of a thermal characteristic (the heat capacity) and a dynamical indicator (the largest Lyapunov exponent) when the parameters of the many-body interaction increase. Our results can be summarized as follows: (1) Similar to the results on the bulk obtained by Baskes, the melting point is reduced as either A or β increase; (2) decreasing the range $1/\beta$ of the many-body term leads to a significantly reduced latent heat of melting; and (3) the dynamics exhibit a more chaotic character when the many-body forces increase or when they get more localized, the variations of the largest Lyapunov exponent being correlated with the heat capacity curves.

In order to calculate the caloric curves and the heat capacities, we have carried out series of Monte Carlo (MC) simulations improved by parallel tempering.¹⁷ The method of parallel tempering allows one to accelerate the convergence of MC simulations by performing simultaneously all the trajectories at different temperatures $\{T_k\}$, and by attempting occasional exchanges between two close temperatures T_i and T_j . If the current configurations denoted $\mathbf{R}_i$ and $\mathbf{R}_j$ have the respective energies $E_i=E(\mathbf{R}_i)$ and $E_j=E(\mathbf{R}_j)=E_i+\Delta E$, then the exchange between the configurations is accepted with the probability

$$\text{acc}(\mathbf{R}_i \rightleftharpoons \mathbf{R}_j) = \min\{1, \exp[\Delta E(1/k_B T_i - 1/k_B T_j)]\}. \quad (7)$$

Parallel tempering Monte Carlo (PTMC) differs from the parallel jump-walking method¹⁸ in that the higher temperature trajectories are also affected by the exchange. See Ref. 19 for a discussion relative to the differences and similarities between the parallel tempering and jump-walking methods.

PTMC has been previously employed in a global optimization context,²⁰ and also recently for studying cluster thermodynamics in difficult cases.¹⁹ One of its most valuable properties is that it does not induce any extra computational cost with respect to standard simulations. The MC simulations are carried out during 10^6 sweeps following 10^5 thermalization sweeps, starting from the global minimum. The potential-energy distributions are calculated, and the caloric curves are computed using a multiple histogram reweighting analysis. The largest Lyapunov exponent λ is also calculated as a function of the total energy E from classical (isoergic) molecular dynamics (MD) simulations. Hamilton's equations of motion are solved by a constant time step four-point Runge-Kutta integration scheme. Using the reduced Lennard-Jones units of energy ε , distances $2^{1/6}\sigma$, and mass m , the time step for integration is chosen as 10^{-3} , the total integration time being 2×10^5 steps at each energy. Initial conditions are chosen as the geometry of the global minimum, with no angular momentum. The maximal Lyapunov exponent λ measures the exponential rate of divergence between two MD trajectories initially close in phase space. We calculate it with the tangent space method.²¹ In addition, we have checked that the caloric curves obtained from MD were consistent with those extracted from MC simulations.

The two sizes studied here are, respectively, the trimer and 13-atom clusters. While the smaller size illustrates the

strong chaotic dynamics, the larger cluster exhibits clear solidlike and liquidlike phases and changes between these phases in a range of temperatures. For these two sizes, the constant Z_0 is taken as $Z_0=N-1$, and the parameter A is varied in the range $0 \leq A \leq 0.6$ while β is increased from 1.2 to 8.5. In all cases, the ground state of the trimer is always the equilateral triangle ($E=-3\varepsilon$), and the 13-mer has the shape of a perfect icosahedron. Upon increasing A above about 0.7, we have observed that the Baskes potential leads to fragmented structures. This can be interpreted as the result of too large average densities $\{\bar{\rho}_i\}$ in the compact geometries, which penalize the many-body terms. In the following, we focus on some values of A , namely, $A=0$ (pure LJ interaction), 0.2, 0.4, and 0.6, and also on some values of $\beta=1.2$ (longest range), 4.2, 6.3, and 8.5 (shortest range). To prevent evaporation from occurring at high temperature or energies, we have also enclosed the clusters in a continuous repulsive spherical wall of the form $\alpha(r_i-r_0)^4/4$, with the radius $r_0=2.5$ reduced units and with $\alpha=100$ units.

The heat capacities for the two sizes, and their variations with A or β have been represented in Fig. 1. All curves show a clear bump, which indicates isomerization for the small cluster, and melting for the larger cluster. In the case of $N=3$, the onset of isomerization occurs near $T_{\text{melt}} \sim 0.2\varepsilon k_B^{-1}$, when the energy fluctuations become large enough so that the linear saddle point can be crossed. As concerns the larger cluster, the definition of a liquidlike phase is no longer ambiguous, and the heat capacity peak centered near $T_{\text{melt}} \sim 0.29\varepsilon k_B^{-1}$ has been recognized as the precursor to the first-order solid-liquid transition in the bulk.²² The effect of the many-body interaction is qualitatively the same for both sizes: Increasing the magnitude A or the range β^{-1} results in a lower melting point T_{melt} , i.e., a lower value of the temperature at which the heat capacity C_V is maximal. However, we observe only a very small effect of changing A for the trimer. This should be attributed to the fact that neither the ground state nor the saddle point are much affected by the many-body terms for the value $\beta=1.2$. On the contrary, increasing β at fixed $A=0.4$ lowers T_{melt} more significantly, by up to 20–25 % for $\beta=8.5$. This situation is also observed for $N=13$, even more clearly because of the narrower peak. The effect of increasing A is stronger, but still results in a decrease of the melting point by about 20% for $A=0.6$. Again, increasing β has the consequence of a lower melting point, which reaches $T_{\text{melt}} \sim 0.24\varepsilon k_B^{-1}$ for $\beta=8.5$.

This effect of lowering the melting temperature is in good agreement with the observations of Baskes in the condensed phases.¹⁰ It is also consistent with the finding that too large values of A lead to spontaneous fragmentation, the isomers belonging to the “liquidlike” phase being not as compact as the solidlike icosahedron, and their energies relative to the ground state getting lower and lower as A increases. Increasing β also reduces the energy difference ΔE between the two lowest-energy isomers: when $A=0.4$, $\Delta E=2.424\varepsilon$ for $\beta=1.2$, and $\Delta E=2.139\varepsilon$ for $\beta=8.5$. These energy gaps are correlated to the shift in the melting temperature.

In the range of A investigated here, the many-body term is essentially repulsive, and smaller than the attractive pairwise term. Following the results of Berry, Wales, and co-workers¹¹ on Morse clusters, we thus expect that decreas-

FIG. 1. Variations of the canonical heat capacities $C_V(T)$ vs temperature for several values of the parameters A and β , extracted from parallel tempering Monte Carlo simulations and histogram reweighting. Upper panels, results for $N=3$; lower panel, results for $N=13$. Left panels, results for increasing A ; right panels, results for increasing β .

ing the range of the many-body potential will lead to a decrease of the number of stable isomers, and to an increase of the volume of accessible configuration space in the liquidlike region. This is consistent with the decrease of the melting point in Fig. 1. As noted by Moseler and Nordiek,¹⁵ this change in the proportion of the configuration space minima belonging to the liquidlike phase also influences the height of the heat capacity peak. Indeed, the latent heat of melting L , estimated by the surface area below the peak, regularly decreases as the range of the electron density increases. This effect is comparatively more important than the shift in T_{melt} , as L drops by nearly 50% for $\beta=8.5$. Interestingly, the form of the Baskes potential, in the range of parameters investigated here, does not seem to lead to any qualitative change in the thermodynamical behavior of the larger cluster, whereas some premelting phenomena may come along with potentials having a soft repulsive core.¹⁶

We now come to the nonlinear dynamics of these clusters, illustrated in Fig. 2 with the variations of the largest Lyapunov exponent λ versus total energy. When $A=0$, the trimer is a pure LJ cluster, and we observe a maximum at $E=1$ and the additional stability prior to the cluster dissociation. By adding a higher complexity to the dynamics, we expect that increasing A will also result in a larger Lyapunov exponent. However, we only see a very small shift of the curves obtained at $A=0$ toward the lower energies as A reaches 0.6. After the saddle point is crossed, there is even a small decrease of λ with increasing A . This result is in accordance with previous findings on triatomic clusters with three-body interactions.^{23,24} In this case, there is an additional near-integrability around the saddle point which is also observed in quantum mechanical analysis of the eigenvalue spectra.²⁴ On the other hand, the effect of β on the Lyapunov exponent is more pronounced, with a larger shift toward the

low energies. This effect is directly related to the change in the energy landscape, the saddle point having a lower energy as β increases. In the case of $n=13$, we see again that the chaotic behavior is nearly independent of the strength of the many-body interactions. Also similar to the trimer case, β affects the dynamics more radically by shifting the curves toward the low energies. Concerning the $n=13$ cluster, previous works have reached different conclusions on the correlation between melting and the variations of the Lyapunov exponents.^{25,26} In fact, while there is a general agreement that bulk systems should exhibit a sharp jump of the largest exponent at melting,^{25,27,28} most simulations tend to indicate that the variations are very progressive^{25,29–31} due to dynamical coexistence.²⁵ For $n=13$, the Lyapunov exponents do not display any sharp change at melting, but their variations with energy are shifted in the same way as the heat capacity.

The present results also show fundamental differences between the Baskes and Morse potentials, since increasing the range of the electron density has the opposite effect on the latent heat as increasing the range of the Morse potential.^{11,15} This mostly comes from the repulsive character of the many-body part of the Baskes potential. Obviously, the Baskes potential should exhibit a much larger variety of behaviors than the simple, single-parameter Morse potential, and also than other embedded-atom models such as Gupta or Sutton-Chen potentials. Although it was initially proposed for bulk phases, it could be suitably adapted for clusters, provided that the parametrization is carefully performed, not only on the bulk, but also on finite size systems.³² In particular, it would be interesting to know if it predicts multistep melting like most other potentials, or if they are some ranges of its parameters where melting is a one-step process similar to what is currently seen in experiments.²

In conclusion, we have studied the dynamical and thermo-

FIG. 2. Variations of the largest Lyapunov exponent $\lambda(E)$ vs total energy for several values of the parameters A and β , extracted from classical molecular dynamics simulations. Upper panels, results for $N=3$; lower panel, results for $N=13$. Left panels, results for increasing A ; right panels, results for increasing β .

dynamical behaviors of small atomic clusters bound by the Lennard-Jones embedded-atom potential developed by Baskes. We have calculated the caloric curves from MC simulations and histogram reweighting. The chaotic dynamics was investigated with the largest Lyapunov exponent λ extracted from classical MD simulations. We have found a general agreement between the thermodynamics and chaotic dynamics of the 3- and 13-atom clusters, namely that increasing the magnitude or decreasing the range of the many-body interactions results in a decrease of the melting point, latent heat of melting, and in anticipated increases of λ .

These results are also consistent with the results of Baskes on the bulk.

The two examples chosen have shown the strong influence of the many-body forces on the energy landscapes, via the thermodynamic behavior related to the relative energy of the low isomers, and via the chaotic dynamics near the saddle points. Considering the possible large experimental variations of both the melting temperature and latent heat of melting as the size changes, we believe that the Baskes potential, with its tunable many-body part, could profit to the theoretical study of the thermal properties of metal clusters.

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