Z. Phys. D 26, 391–393 (1993)

Atoms, Molecules
Zeitschrift für Physik D and Clusters

Chaotic dynamics and vibrational mode coupling in small argon clusters

The influence of potential energy saddles

Robert J. Hinde* and R. Stephen Berry

Department of Chemistry and the James Franck Institute
The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637, USA

Received 16 September 1992; accepted 19 November 1992

Abstract. We have computed the local Kolmogorov entropy of molecular dynamics trajectory segments near the potential energy saddles of model Ar_3 and Ar_5 clusters. In the case of Ar_3 clusters bound with a Lennard-Jones potential, the local Kolmogorov entropy of the cluster is significantly smaller in the saddle region than in other areas of the potential surface. This behavior indicates an increase in the degree of nearly quasiperiodic motion near the Ar_3 saddle due to the partial decoupling of the cluster's vibrational modes there. Lennard-Jones Ar_5 clusters do not exhibit similar behavior, but Ar_5 clusters bound with a short-range Morse potential do. This suggests that the "regularizing" effect of saddle regions is strongly dependent on the shape of the energy surface near the saddle. From these observations, we can determine which features of the saddle are most important in this respect; the flatness of the saddle region seems to be one such feature.

PACS: 36.40.+d; 05.45.+b

1. Introduction

Research into the chaotic dynamics of chemically relevant Hamiltonian systems has become increasingly active over the past three decades. Interest in the chaotic dynamics of molecules stems in part from the possibility that chaos may provide a mechanism for inducing statistical behavior in molecular systems, for example by facilitating the rapid redistribution of vibrational energy throughout a molecule.

Recent work of ours [1] has shown that in the Ar_3 cluster, the portion of the potential energy surface near the bending saddle (associated with a collinear configuration of the three atoms) plays a crucial role in determining how the degree of chaos in the cluster varies with its total energy. Specifically, we found that the saddle region in Ar_3 can act to channel together neighboring trajectories, thereby reducing the degree of chaos in the cluster. This effect depends strongly on the curvatures of the potential surface near the saddle point.

In this paper, we present the first results of a more comprehensive study of the effects of potential energy saddles on the chaotic dynamics of small clusters. Here we discuss the clusters Ar_3 and Ar_5; the complete set of results for 3- through 7-atom clusters will be presented elsewhere [2].

2. Computational method

The Kolmogorov entropy [3] (K-entropy) of a dynamical system quantifies the degree of chaos in the system. The K-entropy of a system can be intepreted as asymptotic long-time rate of stretching of small volumes of phase space. Here we are interested in the *local* K-entropy, which is the finite-time analog of the K-entropy and measures the stretching of phase space along a short trajectory segment.

We generate molecular dynamics (MD) trajectories for a cluster using the standard velocity Verlet method [4] with an integration time step of $\Delta t = 10^{-14}$ s. We periodically quench the cluster in order to determine whether a given trajectory segment remains in the potential well or crosses over a saddle. For each segment of the MD trajectory, we compute the local K-entropy K using standard Jacobian techniques [1]. The trajectory segments we consider here are 1500 time steps long, while the length of the entire trajectory is on the order of 10^6 steps. Hence we obtain between 10^2 and 10^3 values of K, which we use to construct probability distributions.

We will be interested in analyzing the trends in K in terms of the coupling among the vibrational modes of our clusters. We quantify this coupling by defining the instantaneous coupling between two local normal modes:

$$b_{jk} = \hat{\mathbf{u}}_k \cdot \mathrm{d}\hat{\mathbf{u}}_j/\mathrm{d}t\,,$$

where the vectors $\{\hat{\mathbf{u}}_j\}$ are the $3N-6$ local normal modes of an N-atom cluster, which are obtained by diagonalizing the cluster's instantaneous Hessian matrix. This definition is adapted from the work of Miller et. al. [5]. We then define

* Address after 1 January 1993: Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853, USA

the "total" coupling C to be the rms average of the coupling elements $\{b_{jk}\}$:

$$C = \left(\sum_{j \neq k} b_{jk}^2 / (3N-6)(3N-7) \right)^{1/2} .$$

The coupling elements $\{b_{jk}\}$ and the quantity C measure the vibrational coupling at a single time step; to examine the coupling over a trajectory segment we simply average C over the 1500 time steps in the segment. This average is denoted $\langle C \rangle$.

Next we define a quantity which measures how flat the potential surface is near a saddle. Let ω_1^2 be the smallest (nonzero) eigenvalue of our cluster's instantaneous Hessian matrix. If the cluster is in a region of the potential surface with negative curvature, ω_1^2 is negative and the corresponding vibrational frequency ω_1 is imaginary. We average ω_1^2 over a trajectory segment and take the square root to obtain $\langle \omega_1^2 \rangle^{1/2}$, which measures the average instantaneous frequency ω_1 of the cluster. This quantity is generally imaginary, and its magnitude measures how sharp the negative curvature is along a particular saddle.

3. Ar_3 results

In Fig. 1 we show probability distributions for K, $\langle C \rangle$, and $\langle \omega_1^2 \rangle^{1/2}$ for an Ar_3 cluster with total energy $E = -1.85\,\epsilon$ bound by pairwise Lennard-Jones potentials. For this cluster, the atomic mass m = 39.948 amu, σ = 3.405 Å, and ϵ = 121 K. The minimum energy configuration has energy $E = -3.00\,\epsilon$; the saddle point is at $E = -2.031\,\epsilon$.

We see that the local K-entropy accumulated by the cluster in the saddle region is substantially lower than that accumulated in the potential well. In addition, the mean vibrational coupling $\langle C \rangle$ is much lower near the saddle. These observations suggest that, in the saddle region, the Lennard-Jones Ar_3 cluster behaves approximately like a set of three uncoupled oscillators. Hence the cluster's motion is largely quasiperiodic as it passes over the saddle; this is reflected in the low values of the local K-entropy in the saddle region. Examination of the individual coupling elements $\{b_{jk}\}$ and of the actions associated with the cluster's vibrational modes show that the separation of the modes is in fact quite good near the saddle [2].

We also note that the mean negative curvature in the saddle region is significantly lower than that in the potential well, as is indicated by the low magnitude of $\langle \omega_1^2 \rangle^{1/2}$ near the saddle. This suggests that the saddle is long and flat when compared with the potential well. In Sec. 5 we will discuss further the connection between the shape of a saddle and its ability to decouple a cluster's modes. It may at first glance seem surprising that trajectory segments in the well sample regions of the potential surface which are strongly negatively curved. This result is not so puzzling, however, if we remember that at $E = -1.85\,\epsilon$ the MD trajectory can explore areas high on the sides of the potential well, where there is substantial negative curvature along the stretching modes.

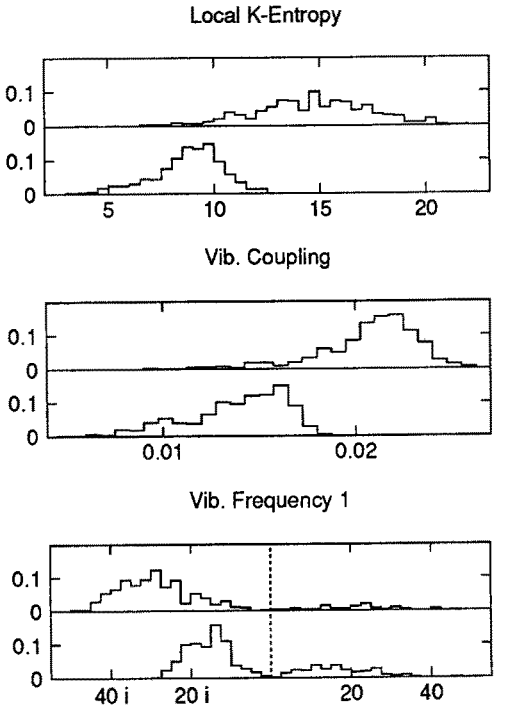


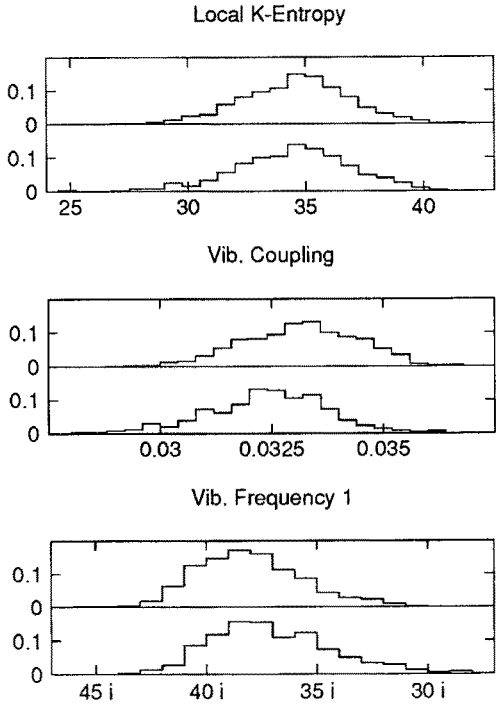
Fig. 1. Probability distributions for K, $\langle C \rangle$, and $\langle \omega_1^2 \rangle^{1/2}$ for a 3-atom Lennard-Jones cluster at total energy $E = -1.85\,\epsilon$. The upper distribution in each pair corresponds to trajectory segments residing completely in a single potential well; the lower distribution corresponds to segments which pass over the saddle connecting two wells. Each distribution is normalized to unit area. Units for the abcissae are: K-entropy, bits/10^{-11} s; vibrational coupling, 10^{14} s^{-1}, vibrational frequency, cm^{-1}

4. Ar_5 results

In Fig. 2 we show similar probability distributions for a Lennard-Jones Ar_5 cluster with total energy $E = -7.0\,\epsilon$. Here we find that the potential in the saddle region is not effective at decoupling the cluster's vibrational modes, and so the local K-entropy accumulated in the saddle region is comparable in magnitude to that accumulated in the potential well. We also see from Fig. 2 that in Lennard-Jones Ar_5, the saddle region and the potential well are both significantly negatively curved.

In the Morse Ar_5 cluster, however, we see very different behavior. Figure 3 shows the probability distributions for K, $\langle C \rangle$, and $\langle \omega_1^2 \rangle^{1/2}$ for a 5-atom Morse cluster with total energy $E = -7.0\,\epsilon$. The diatomic Morse potential binding this cluster together has the same well depth and equilibrium bond length as the Lennard-Jones potential we used to model Ar_3 and Ar_5. However, we have set the dimensionless range parameter [6] of the Morse potential to $\rho = 9$, so that the attractive tail of the diatomic Morse curve falls off to zero much faster than that of the Lennard-Jones curve. (The Morse and Lennard-Jones pair potentials are similar if the Morse parameter $\rho = 6$.)

This change in the cluster's potential energy surface recovers the general pattern of behavior we found for Lennard-Jones Ar_3: the saddle region once again acts to partially de-



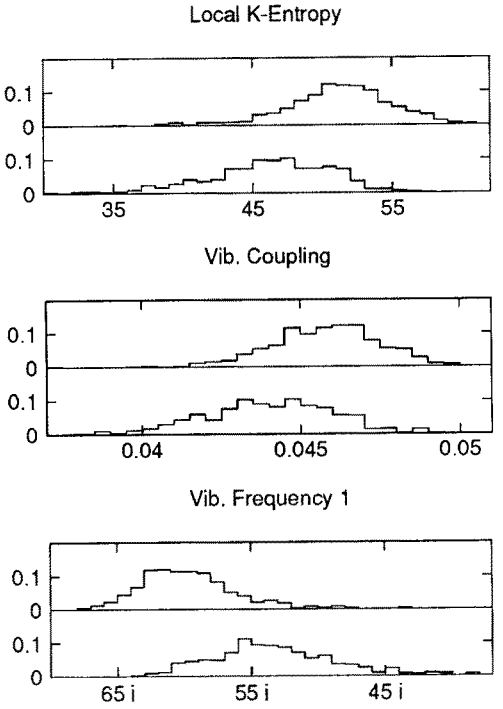


Fig. 2. As in Fig. 1 except for a 5-atom Lennard-Jones cluster at total energy $E = -7.0\epsilon$

Fig. 3. As in Fig. 2 except for a 5-atom cluster bound by short-range Morse potentials instead of Lennard-Jones potentials

couple the cluster's vibrational modes, and the approximate quasiperiodicity that results manifests itself in lower values of the local K-entropy in the saddle region. We also find that in the Morse Ar_5 cluster, as in Lennard-Jones Ar_3, the saddle region is substantially flatter than the well.

5. Discussion

It appears that the ability of a potential energy saddle to temporarily decouple a cluster's vibrational modes depends strongly on the flatness of the saddle. The Lennard-Jones Ar_3 cluster we studied here has a very flat saddle: at the saddle point, the vibrational frequency of the single negatively-curved mode, ω_s, is only $7.32\,i$ cm^{-1}.

The five-atom clusters we have studied each have two important saddles: a low-lying diamond-square-diamond (DSD) saddle, and a higher-energy edge-bridging (EB) saddle. Both of these saddles are accessible at $E = -7.0\,\epsilon$ for the two Ar_5 clusters studied here, and Figs. 2 and 3 contain data for both kinds of saddle. The two saddles in Lennard-Jones Ar_5 are fairly sharply curved, with $\omega_s = 35.52\,i$ cm^{-1} (DSD) and $\omega_s = 18.84\,i$ cm^{-1} (EB). In the Morse Ar_5 cluster, the saddles are somewhat flatter: $\omega_s = 30.31\,i$ cm^{-1} (DSD) and $\omega_s = 8.64\,i$ cm^{-1} (EB). (The energies of the Ar_5 saddle points are reported elsewhere, where we consider the dynamical effects of each kind of saddle separately [2].)

It is reasonable to suggest that flat saddles are more effective at decoupling a cluster's vibrational modes. If a saddle is very flat, then the shape of the potential surface changes quite slowly as we cross the saddle, leading to good separation of the vibrational modes there. A sharply curved saddle is not as effective in decoupling vibrational modes because as we cross the saddle the potential surface changes more quickly, both in the saddle-crossing mode and in the directions with which that mode couples. The results presented here show that the saddles of Lennard-Jones Ar_3 and Morse Ar_5 (with $\rho = 9$) are sufficiently flat to partially decouple their respective vibrational modes. The saddles of Lennard-Jones Ar_5, however, are too sharply curved to effectively decouple the modes of this cluster; hence the local K-entropy accumulated near the saddles is comparable to that accumulated in the potential well.

References

1 Hinde, R.J., Berry, R.S., Wales, D.J.: J. Chem. Phys. **96**, 1376 (1992)
2 Hinde, R.J., Berry, R.S.: in preparation
3 Kolmogorov, A.N.: Dokl. Acad. SSSR **124**, 754 (1959)
4 Heerman, D.W.: Computer Simulation Methods in Theoretical Physics (2nd ed). New York: Springer 1990
5 Miller, W.H., Handy, N.C., Adams, J.E.: J. Chem. Phys. **72**, 99 (1980)
6 Braier, P.A., Berry, R.S., and Wales, D.J.: J. Chem. Phys. **93**, 8745 (1990)

This article was processed using Springer-Verlag TEX Z.Physik D macro package 1.0 and the AMS fonts, developed by the American Mathematical Society.