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Noble Gas Clusters in Model Zeolite Cavities

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Abstract. Noble gas atoms trapped in the intracrystalline cavities of zeolites may form clusters. A classical-mechanical isoenergetic molecular dynamics simulation is performed to simulate the dynamical behavior of noble gas clusters in zeolite cavities. To implement the simulation, a model is adopted of a homogeneous spherical cavity with Morse interaction between the noble gas atoms and cavity walls. The results for Ar_6 clusters indicate that the noble gas clusters in the cavity undergo the same solid/liquid phase changes as in free space, and, at high enough energies, a rapid exchange between atoms adsorbed on the inner surface and thosein the interior of the cavity. Mathematical quenching is used to investigated the multidimensional potential surface of Ar clusters in the cavity.

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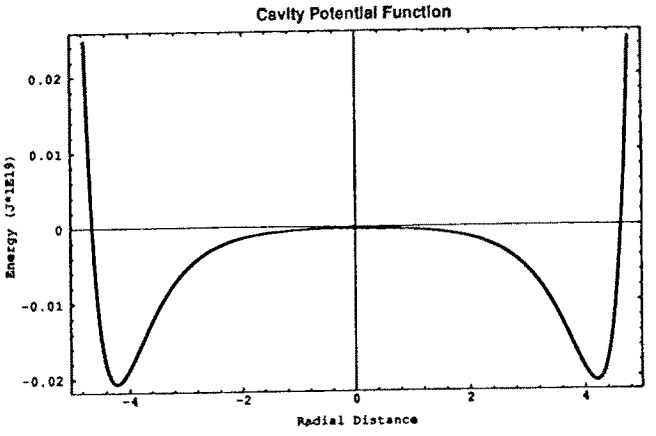
Fig. 1. Potential function between Ar and the cavity. The radius of cavity is 6.5 Å; the minimum is at 4.38 Å, and in this example the interaction of Ar-cavity is approximately equal to the interaction of Ar-Ar.



1. Introduction

Noble gas atoms have been used as probes for investigating microporous materials, especially ^{129}Xe in zeolites, but the dynamical behavior of the noble gas atoms in those materials remains an open and challenging problem. Results from several experiments [1,2] show that, in high loadings, the noble gas atoms trapped in may intracrystalline cavities of zeolites may form clusters, and the interaction between noble gas atoms plays an elusive role. A "rapid exchange model" developed by Cheung et al. [3] indicates that the noble gas atoms in gas phase within the zeolite may undergo rapid exchange with those adsorbed on the surface. This phenomenon, sometimes called a gas/liquid phase coexistence, may be similiar to the solid/liquid phase coexistence of free clusters, especially in experiments performed at low enough temperature that the trapped atoms are not necessarily gas-like. The dynamical behavior of small noble gas clusters in free space has been well understood, largely through analytic theory and simulation techniques [4]. Armed with these, we may unravel this mystery.

In this paper, we present some preliminary results of a more comprehensive study of the dynamics of noble gas atoms in zeolite cavity. Here we discuss the clusters Ar_6; the complete set of results for 3- through 7-atom clusters will be presented elsewhere [5].

2. Model and Method

A model zeolite cavity is created as a homogeneous spherical cavity with Morse interaction between Ar and the cavity. Integrating along the inner surface of the cavity, the interaction potential function is shown in Fig. 1. The radius of cavity is chosen as 6.5 Å. The other parameters are adjusted to make the Ar-Ar and Ar-cavity interaction approximately equal. Molecular dynamics (MD) trajectories are generated by using the velocity version of the Verlet method with an integration time step of $\Delta t = 5 * 10^{-15}$ s. The length of a typical trajectory is 2 ns. The minima of the potential surface of the argon clusters are found by periodically quenching the system by the steepest descent quench method [4], and the saddles, by the skiing-down or slowest-slides method [7], and both are identified by the eigenvalues of Hessian matrix. To prevent rotation motion, the initial

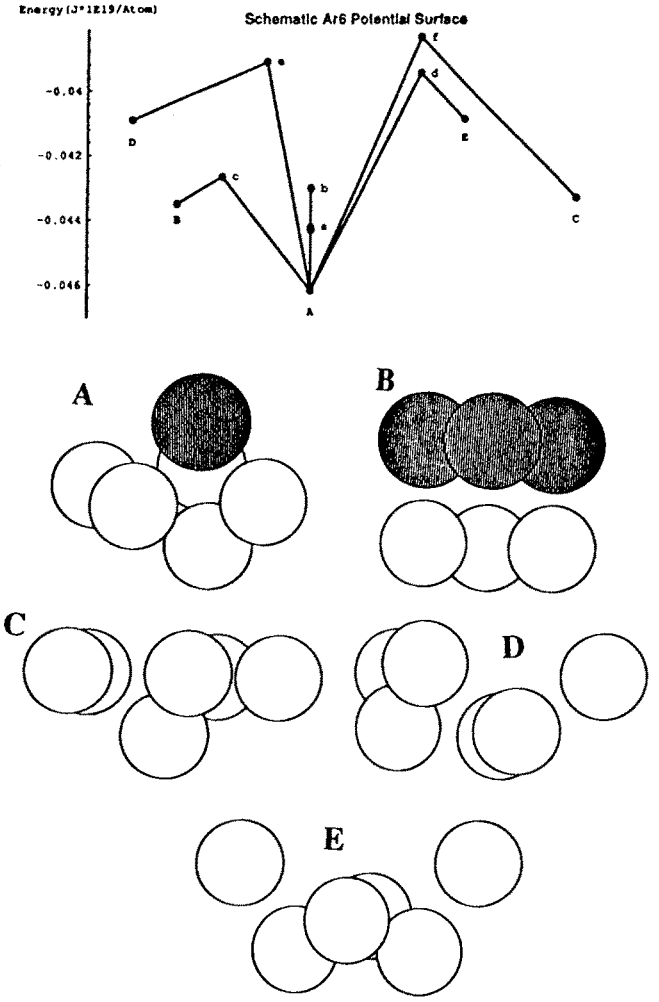


Fig. 2. Schematic potential surface for Ar_6. A,B,C,D,E are minima and a,b,c,d,e,f are saddles. The point a includes three different saddles which have the same energy; a and b are saddles connecting permutational isomers. In the lower part, the white spheres are argons contacting the surface of the cavity, and the shaded spheres contact only the other argons.

configuration is generated by twisting the global minimum, equilibrating and then scaling the velocities to the desired total energy. The simulation diagnostic techniques, such as relative root mean square bond length fluctuation (RMS), mean square displacement (MDS), normalized velocity autocorrelation function, and power spectrum are described in reference 6.

3. Ar_6 results

In Fig. 2, the schematic potential surface and the structures of clusters at their minima are shown. There are 5 minima and 8 different saddles with 4 different permutational saddles for minimum A. The minimum A has one argon not contacting the cavity surface but in contact with the other argons, and B has three such argon atoms.

By slowly increasing the total energy, we are able to investigate the structure changes of the cluster. In Fig. 3, the relative root mean square bond length fluctuation is shown. At low energy, the system cannot pass over any barriers, so the RMS stays small and smoothly increases.

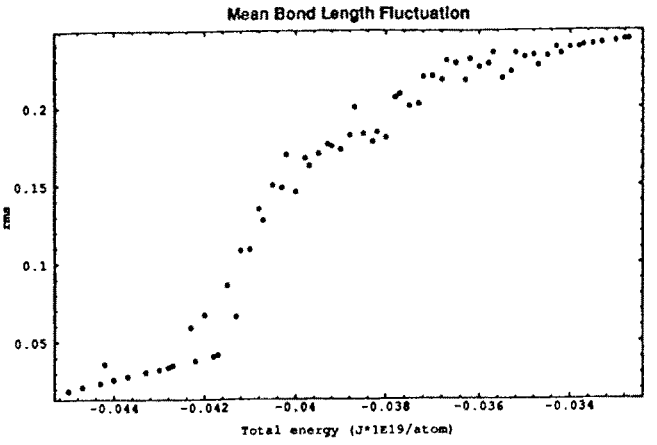


Fig. 3. Mean bond length fluctuation vs total energy. Large fluctuations begins when the system begins to pass over the saddle c. The small fluctuation near -0.044 is caused by permutation among the minima of geometry A; the fluctuations decrease when the energy is above the energy of saddle f.

Above $-0.044*10^{-19}$ J/Ar , the system begins to pass over barriers, and the RMS indicates the fluctuation of structures, especially above $-0.042*10^{-19}$ J/Ar. At high energy, the system undergoes fast interwell motion, so the fluctuation becomes smooth again. At even higher energies, some of the Ar atoms desorb and wander around the cavity. In Fig. 4 we choose 4 different values of energy to show the dynamics of Ar_6 in the cavity.

4. Discussion

There are only 2 minima and 4 saddles for Ar_6 in free space [8], but 5 minima and 8 saddles in our model cavity. The locally and globally stable structures in the cavity are different from those in free space because of the curvature of the cavity and the strength of interaction between argon and the cavity. In this respect, noble gas atoms are effective probes. It appears that noble gas clusters in cavities also undergo solid/liquid phase changes like that found for clusters in free space, but the dynamics is much more complicated since the clusters tumble around in cavities. New simulation techniques are needed to analyze rotational motion.

It is reasonable to suggest that the "rapid exchange model" in larger clusters in zeolites will not only involve the exchange of the noble gas atom in the cavity interior with those absorbed on the surface, but also between different layers, according to structures of minima.

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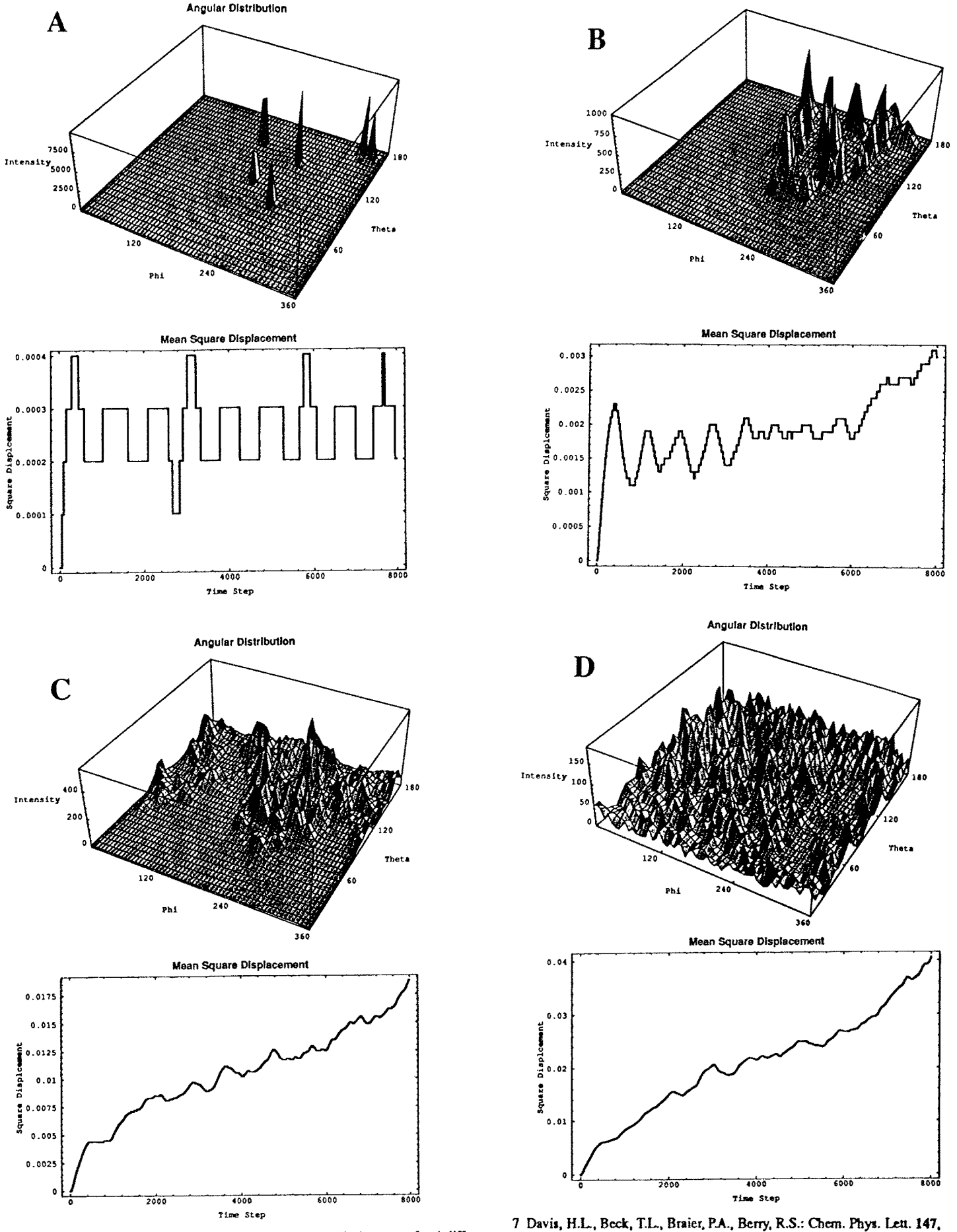

Fig. 4. The angular distribution and mean square displacement for 4 different values of energy, A=-0.045*10^{-19} J/Ar, B=-0.041*10^{-19} J/Ar, C=-0.0386*10^{-19} J/Ar, D=-0.0366*10^{-19} J/Ar. The Ar_6 cluster undergoes the transition from solid-like, solid/liquid coexistence, liquid-like, and gas phase.

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