

Molecular Dynamics Simulation on the Volume of a Sodium Atom in Ar Environment: a Model of Solute Molecule in Solution

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Molecular volume is an elusive concept. Unlike the classical particles, the boundary of molecule is not well defined. Most of the volume of molecule is occupied by the electrons, but the positions, and hence, the volume occupied by the electrons are not definite, following the Heisenbergs uncertainty principle. For pure materials, one may just divide the molar volume of material by Avogadro's number, or one may define the volume by specifying an arbitrary electron density (for example, in Gaussian 94 set of programs,¹ the volume of molecule is "defined" as that inside a surface on which the electron density is 0.01). The first one may suffer from neglecting the volume of vacant site. In the second type of definition, the arbitrariness of the specified electron density may be the problem. For a solute molecule in the solvent environment, similar difficulties arise in the definition of molecular volume. The volume of solute molecule in solution will not be so simple to define, and will depend on the composition of the solution, that is, on the solvent environment around it. Thus, detailed analysis of the configuration of the solvent molecules must be carried out in the vicinity of the solute. In this regard, useful and popular methods based on the polarizable continuum model (PCM),² which regard the solvent as continuous medium represented by macroscopic properties (for example, the dielectric constant), will fail to address these important points.

Recently, much attention has been devoted to the properties of solutions, partly due to the rapidly increasing computational capability and efficient software. Especially, those properties depending on the configuration of solvent molecules around the solute has been the focus in several studies.³ For example, it is well known⁴ that many properties of the solution can be expressed as linear combination of terms one of which depends on the volume of solute molecule. The solute volume in this relation stems from the fact that in the dissolution processes, the solute molecule occupies a cavity and takes apart the solvent molecules to outside the cavity. In order to estimate this "cavitation energy", accurate analysis of solvent environment in the vicinity of solute molecule is necessary. More recently, Cheong and co-workers^{5,6} showed that qualitative argument based on the resonance structures of the solute-solvent systems may not well explain the enthalpies of interaction in benzene derivative – water system, and that the concept of the accessibility of solvent molecules around the solute molecule may be a better tool for understanding their measurements. In order to estimate the solute-solvent accessibility, systematic study should be carried out on the detailed configuration of solvent mole-

cles around the solute.

When a solute is surrounded by solvent molecules, the solute-solvent complex would behave like a "supermolecule" of characteristic electronic structure and vibrational frequencies. The nuclei in the supermolecule complex would move along the potential surface of the electronic state of the system, and the whole supermolecule complex will vibrate around the equilibrium position. Therefore, it is natural to define the volume of a solute molecule in solvent environment as that inside the surface on which the solute-solvent interactions are globally minimum. This definition is unambiguous, because the potential energy would increase (that is, the nuclei repel) when the nuclei in the solute-solvent complex gets inside this surface. Thus, in order to compute the volume of solute, it will be necessary to examine the potential surface of the solute-solvent supermolecule complex near the equilibrium configuration of the nuclei. This approach will also give detailed knowledge on the configuration of solvent molecules near the solute, rendering important information such as the solute-solvent accessibility.

In this work, we present a molecular dynamics simulation of a sodium atom in argon matrix (approximated by 24 Ar atoms) in order to introduce and demonstrate this definition of the molecular volume of a solute in solvent environment. Since there exist no experimental results that can be compared with the results in this report, we present the computed results to introduce the adopted definition and to demonstrate the methods of direct dynamics employed here. We consider the Na-Ar₂₄ system as a supermolecule, and treat the system in the spirit of *direct dynamics*, which directly computes the potential energy surface and the resulting forces exerted on the nuclei of the system at each of the nuclear configurations, simultaneously with molecular dynamics simulation. The nuclei move thereby, according to the forces, and computations are carried out at the new configuration, etc. We model the system as mixed quantum-classical one: We treat⁷ the valence electron of the sodium atom explicitly in quantum mechanical way (by employing angularly nonlocal effective core potentials^{7(a)} for electron-Na⁺ and electron-Ar interactions), and employ core-core interactions (in the form of Lennard-Jones potentials) for the Na⁺ core and the Ar atoms, including polarization (for details and parameters, see Ref. 7(a)). The 48 floating Gaussian basis functions are employed to compute the wave function of the valence electron of Na. The forces are computed at each nuclear configuration, and molecular dynamics simulation is carried out, letting the nuclei move following these forces



Figure 1. Snub cube.

(for details, see Ref. 7). Verlet algorithm is employed to carry out the propagation. We assume that the 24 Ar atoms surround the Na atom in snub cube and carry out simulation under this constraint. Of course, there is no guarantee that the arrangement of Ar atoms around the Na atom in matrix environment is snub cube. The Na atom may be located in tetragonal or octagonal site, or in other arrangements. However, although several investigators measured⁸ optical spectra of Na atom in Ar matrix, the absorption bands have not been assigned to specific trapping sites yet. Therefore, it is not clear how the Ar atoms are located around the Na atom, either in Ar matrix or in liquid Ar. We assume here the snub cube arrangement in order to demonstrate the definition of the volume of solute molecule adopted here, and to show the typical system that can be treated. We arrange the 24 Ar atoms around the Na atom in snub cube fashion, and scan the Na-Ar distance.

We computed the potential energy as a function of the Na-Ar distance as shown in Figure 2. It can be seen that the minimum-energy snub cube arrangement is obtained at $R_{\text{Na-Ar}} = 9.535$ bohr (5.046 Å), which can be defined as the radius of Na atom in Ar matrix (in snub cube arrangement). The shape of Na atom here is spherical, because the valence electron is in s-orbital and the 24 Ar atoms are located in symmetrical fashion. The $R_{\text{Na-Ar}}$ obtained here is a bit smaller than the Na-Ar distance (5.59 Å) in NaAr diatom^{7(a)} computed by the same mixed quantum/classical simulation. Although detailed estimation of the free energy must be carried out to compare the relative stability, it seems that the other 23 Ar atoms seems to stabilize the Na-Ar bond to shorter Na-Ar distance. The total binding energy of the cluster in snub cube arrangement is computed to be 6993 cm^{-1} .

For more complex systems (polyatomic solute in solution), more elaborate simulations would be necessary, because

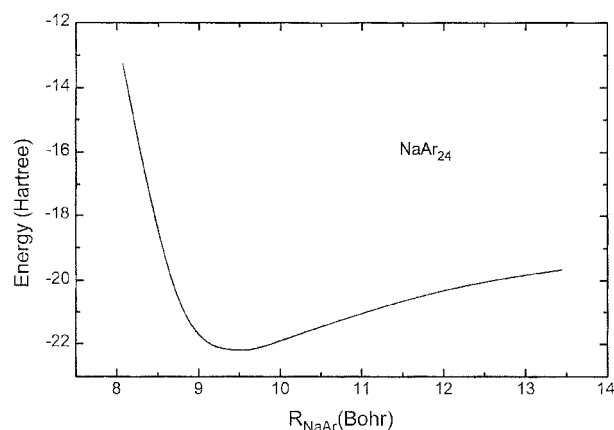


Figure 2. Potential curve of snub cube NaAr₂₄ as a function of NaAr distance.

the solute is not spherical in this case. Since detailed analysis must be carried out on the global minimum energy configuration of solvents in the vicinity of solute, at least several solvent molecules must be explicitly treated. More analysis will be reported in future publications.

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