Journal of Molecular Structure: THEOCHEM 852 (2008) 22–29

THEO
CHEM

www.elsevier.com/locate/theochem

A comparison of interatomic potentials for rare gas nanoaggregates

Andrea Lombardi [*], Federico Palazzetti

Dipartimento di Chimica, Universitá di Perugia, I-06123 Perugia, Italy

Received 31 October 2006; received in revised form 11 May 2007; accepted 7 October 2007
Available online 23 December 2007

Abstract

Rare-gas clusters are usually modeled by Lennard–Jones pairwise potential energy functions. A more realistic representation of the rare-gas pair interaction is given by the benchmark Aziz HFD type potentials, of high computational cost for large scale molecular simulations. Here we compare Lennard–Jones and HFD potentials with that obtained from a generalization of the Lennard–Jones potential, recently presented by Pirani et al. Parameters are given for the two-body interaction for all dimers and structural properties of Ar_5 and Ar_6 are discussed through a comparison of the Pirani et al. potentials with those of Lennard–Jones.

Keywords: Potential energy surface; Minimum energy configuration; Saddle point; Long-range interactions

1. Introduction

Prototypical systems exhibiting phenomena of relevant interest for the wider class of many-body systems, rare-gas clusters are studied for various sizes by simulations under different conditions, such as high and low temperatures, supercooled conditions, in undergoing phase transitions, or as crystals or glasses [1–8]. Lennard–Jones clusters are rare-gas aggregates modeled through a Lennard–Jones (12-6) two-body potential function leading to a simple parametrization of the Potential Energy Surface (PES) and to a simple analytical gradient function of small impact on the computational cost of large simulations. The many-body Lennard–Jones PES with many local minima are also used as a testing ground for minimum search algorithms. We have studied structural and dynamical properties, phase transition and specific heats [5–8].

The Lennard–Jones two-body potential function, satisfactorily reproduces the two-body rare-gas interaction in the well region, but does not accurately describe the short-range repulsion (too repulsive) and the long-range attraction, which is overestimated. It is well known that apparently negligible differences in the two-body potential profile can result in significant differences in the shape of the PES also locally, such as at saddle points, where important features of the cluster dynamics originate. This has been clearly shown for small clusters, e.g. in Ref. [9] by Hinde and Berry.

Concerning large clusters, the long-range interactions between atoms are important, due to the large size of these systems, and in general these long-range dispersion forces are crucial in many chemical and biological systems. As an example one could cite the double helix DNA structure, or large chain molecules, or even bulk systems.

For these reasons, the Lennard–Jones simple repulsion–dispersion interaction model is poorly adequate for studies aiming at the validation of models through comparison of simulated dynamical and thermodynamical properties with experimental data.

A more realistic description of the two-body interaction would require quantum mechanical approaches, as in the case of Tang-Toennies and Aziz two-body potentials for rare-gas atoms [10–16], which are indeed more accurate, but at the price of a higher number of parameters involved in the potential function, that increases the computational cost of large scale simulations.

Recently, Pirani et al. [17] proposed a generalization of the Lennard–Jones potential function introducing in the

---

[*] Corresponding author. Tel.: +39 075 5855511; fax: +39 075 58555606.
E-mail address: abulafia@dyn.unipg.it (A. Lombardi).

0166-1280/$ - see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.theochem.2007.12.011

exponent of the repulsive term a dependence on the reduced distance, following and improving a previous similar attempt by Maitland and Smith [18]. The new parameterization significantly improves the flexibility and the accuracy of the potential both in the short and long-range region and still maintains the ease of computing.

In the present paper, we analyze the atom–atom interaction for the entire rare gas series. In particular we compare Lennard–Jones, Aziz and Pirani et al. two-body potential functions focusing onto three parts of the potential energy profile, the short-range repulsive region, the well region and the long-range attractive region. This is according to the fact that different regions play different roles in contributing to the dynamics and thermodynamics of the clusters under different conditions. A comparison of the minima and saddle points of the Pirani PES of Ar_5 and Ar_6 clusters is also made with those of the Lennard–Jones PES [19,20].

The plan of the paper is as follows. In Section 2 the main features of the Aziz, Lennard–Jones and Pirani et al. potentials are sketched. In Section 3 the Ar_5 and Ar_6 potential energy surfaces are presented along with the structural properties of Ar_5 and Ar_6, as obtained using Lennard–Jones and Pirani et al. potentials. In Section 4 the comparison of the potentials of the rare gases, using the three previous formulations, is reported [14,16,21–23]. Conclusions follow in Section 5.

2. Interaction potentials

2.1. Semiempirical potentials

The most widely used empirical and semiempirical potentials for rare-gas dimer interactions are based on the so called Hartree–Fock-Dispersion model (HFD). Within this model the interaction energy (U_{int}) between the two closed shell rare-gas atoms is represented as the sum of two terms denoted hereinafter as U_{SCF} and U_{COR}.

U_{SCF} represents the Self-Consistent-Field Hartree–Fock repulsion between the closed shell atoms, obtained by ab initio calculations. U_{COR} accounts for both the dispersion energy coming from the instantaneous dipole–induced dipole interactions and the modulation of the dispersion energy due to charge cloud overlap, by means of damping functions included in the term.

The HFD representation involves various adjustable parameters in both terms and it is therefore flexible to fit experimental data, such as rotovibrational spectra or molecular beam scattering data.

Several variants of the model have been proposed, during the last decades, to reproduce and interpret new and better quality experimental data, as they become available. To date, the Aziz HFD-B potential model [13,24,25] (a modification of a model previously proposed by Douketis et al. [13]) in its version for Ne [22], Kr [14] and Xe [23] pair interactions, is probably the most referenced pair-potential in the literature for these systems. Further improvements of the HFD-B model, by the introduction of individual dumping functions in the dispersion series, have led to the HFDID potentials, which are referenced for He [21] and Ar [16] pair interactions. In recent years, potential calculated completely ab initio have been significantly improved, in the effort of extending them to larger weakly bound systems [26].

In the study of rare-gas dimers interaction we used a class of such potentials, mainly due to Aziz et al., to be compared with the Lennard–Jones and the Pirani et al. potentials; most of them were validated by experimental data interpretation [16].

It is worth to mention that, besides the above semiempirical representations, it is a common practice to separate into individual terms the total analytical potential function. In general it is convenient a three term partition: short-range by a Morse-like function, the attractive well and the long-range part. The parts behave in different ways with distance, greatly simplifying the development of the potential.

Let us now briefly outline some detail of the Aziz model.

The interaction energy is as follows:

$$U_{\mathrm{int}} = U_{\mathrm{SCF}} + U_{\mathrm{COR}} \tag{1}$$

where U_{SCF} is the Self-Consistent-Field (SCF) Hartree–Fock interaction energy for rare-gas dimers, often represented as [24,25,27]

$$U_{\mathrm{SCF}} = A\mathrm{e}^{-\alpha R} \tag{2}$$

where R is the interatomic distance and the parameters A and α are obtained fitting a set of energies from SCF calculations at various R.

In an improved version of the HFD potentials (see Eqs (1) and (2)), also known as HFD-B [14,15,28], U_{SCF} is represented by:

$$U_{\mathrm{SCF}}(\text{HFD-B}) = A\mathrm{e}^{(-\alpha R+\beta R^2)} \tag{3}$$

In the single-damped HFD potential model, U_{COR} is represented by the following function:

$$U_{\mathrm{COR}} = -\left(C_6R^{-6} + C_8R^{-8} + C_{10}R^{-10}\right)F(R) \tag{4}$$

where

$$F(R) = \mathrm{e}^{[-(DR_{\mathrm{m}}R^{-1}-1)^2]}, \quad R < DR_{\mathrm{m}} \tag{5}$$

$$= 1, \quad R \geqslant DR_{\mathrm{m}} \tag{6}$$

where R_{m} is the minimum energy distance.

Generally, A, α, β and D, as well as the dispersion coefficients C_n, ($n = 6$, 8, 10) are determined by fitting the energy values (ab initio if available) to the chosen HFD mathematical form, the testing ground for the obtained function being the calculation of measurable quantities characteristic of the system, through which the above parameters can be also adjusted. For a complete account of this subject and extensive referencing see Ref. [29].

2.2. Lennard–Jones two-body potential

The Lennard–Jones potential function (see Fig. 1) describes the interaction between two neutral atoms or