Adsorption (2008) 14: 727–732
DOI 10.1007/s10450-008-9110-4

# Direct calculations of the dispersion interaction between fullerenes and their equation for the potential energy

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Received: 16 April 2007 / Revised: 6 January 2008 / Accepted: 8 February 2008 / Published online: 4 March 2008
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**Abstract** A discrete summation method has been developed to calculate the dispersion interaction potential between two $C_{60}$ fullerene molecules and applied to the fullerene–argon and fullerene–helium systems. The pairwise atom-atom potentials for carbon–carbon, carbon–argon and carbon–helium interactions were described by the Lennard-Jones (6-12) expression and considered to be additive. Increased accuracy of these calculations was achieved by accounting for the radius and positions of each carbon atom in fullerene by taking into consideration the irregularity of hexagons in the fullerene structure.

As we understand, a discrete summation method has not been employed for the calculation of the $C_{60}$–$C_{60}$ interaction. Additionally, the method provides a mechanism to calculate the interaction potential for different directions of approach and orientations of fullerene molecules. These differences reach up to 6% at the minimum energy position when comparing approaching hexagons compared to pentagons.

The description of the calculated interaction potential energy of molecular $C_{60}$–$C_{60}$ fullerene that we propose is a physically grounded equation, which has provided excellent fit with the dispersion interaction data. We show that this equation is less complex in structure, while providing a higher accuracy (1% or less inaccuracy) than, for instance Girifalco's (1992) equation, which gives inaccuracy in the range 4–5% when employed on our data. The proposed equation was further modified to provide a successful analytical description of the argon-fullerene interaction energy and an estimate of the resultant Henry constant and isosteric heat of adsorption.

Finally these equations were used to calculate the variation of these Henry constants with temperature for the helium–fullerene system indicating that at room temperature the excess adsorption is negative and that the resulting error when used as a volumetric calibrant, although not unduly significant, is not negligible.

**Keywords** Fundamentals of adsorption · Molecular modelling · Gas phase adsorption

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## 1 Introduction

Fullerenes are beginning to find a diverse range of applications including biomedical (Bosi et al. 2003), antioxidants (Gharbi et al. 2005), bio- and chemical sensors (Giakos et al. 2002), as well as polymer electronics (Wang et al. 2002), superconductivity (Hebard et al. 1991; Pichet 1991), encapsulation noble gases inside the fullerene cages (Saunders et al. 1996) as well as others. The latter applications attach particular significance to the interaction potential inside of the fullerene molecule. This diversity is a consequence of many unique properties of fullerenes.

The dispersion interaction between fullerenes themselves as well as with other molecules plays a substantial role in the characterization of physical, chemical, mechanical, and electrical properties of fullerene containing materials. In addition, an analytic intermolecular potential provides the possibility for more successful investigation of both the phase diagram and the equation of state of these fullerenes.

There are few published studies referring to the dispersion interaction between fullerenes together with a corresponding analytical expression for the intermolecular potential. Initially, Girifalco (1992), using a smeared out spherical approximation, derived an equation for the interaction

potential energy between two fullerene molecules. Sprik et al. (1992) proposed a potential model in which the Lennard-Jones 12-6 interactions between 60 carbon atoms of each molecule of fullerene were supplemented with 30 similar 12-6 sites located at the centres of these double bonds. This potential model was then used in molecular dynamics simulations. Pacheco and Prates Ramalho (1997) computed the dispersion interaction between two and three fullerenes in a time-dependent density functional approach with the Morse potential representing the short-range component and a van der Waals expansion representing longer distances. Girard et al. (1994) deduced only the attractive intermolecular potential between two fullerenes using a discrete-dipole formalism in which $C_{60}$ is viewed as a rigid cluster of 60 polarizable interacting carbon atoms. The dispersion energy was obtained from the shift in the zero-point energy of the ground-state dipolar functions.

## 2 Methodology

### 2.1 Direct calculation of the fullerene–fullerene interaction potential curve

A discrete summation method that takes into account the spherical symmetry of the fullerene itself and the translational symmetry of fullerene–fullerene system similar to that developed for the potential energy distributions arising with carbon nanotubes, has been employed here (Mainwaring et al. 2005). The dispersion interaction potential between two $C_{60}$ fullerene molecules was considered as the sum of the interactions between all of carbon atoms on one molecule with those of the other. However, the interaction potential also depends on the orientation of the approaching fullerene molecules. Here we performed calculations for two cases: molecules approaching each other by similarly oriented hexagons and similarly oriented pentagons along the axis passing through the centres of fullerenes. We also took into account irregularity of the hexagons in $C_{60}$ fullerene. The length of the double bonds is equal to 0.140 nm and the length of the single bonds is 0.146 nm. On this basis that we have calculated the mean ball diameter of $C_{60}$ as $d = 0.7128$ nm.

The discrete summation methodology adopted in the present study represents the potential energy between two approaching and physically interacting carbon atoms of fullerenes by the Lennard-Jones expression

$$U(z_k) = 4\varepsilon\left[\left(\frac{\sigma}{R_{ij}}\right)^{12} - \left(\frac{\sigma}{R_{ij}}\right)^{6}\right] \tag{1}$$

where $z_k$ is the current distance between centres of two fullerene molecules and $R_{ij}$ is the current distance between $i$-th carbon atom of first fullerene and $j$-th carbon atom of the second fullerene. Parameters $\varepsilon$ and $\sigma$ are taken as $7.069 \cdot 10^{-22}$ J and 0.3354 nm respectively (Gray and Gubbins 1984).

The interaction potential between two fullerene molecules was found by calculation of the following double sum, which was performed for $k$ varying from 0 to 1000

$$\mathrm{Sum}(\mathrm{Sum}(U(k,i,j), j = 1 \ldots 60), i = 1 \ldots 60) \tag{2}$$

where, for each $k$, calculations were carried out for each fixed distance $z_k = z_0 + 0.001k$.

Initially the coordinates for each of the 120 carbon atoms were determined using spherical polar system of coordinates. When two fullerenes are approaching via their pentagons, all 60 carbon atoms are located on 8 parallel planes each containing 5, 5, 10, 10, 10, 10, 5, 5 atoms respectively. In the case of approach via their hexagons, all 60 carbon atoms are located on 12 parallel planes each containing 6, 6, 3, 6, 3, 6, 6, 3, 6, 3, 6, 6 atoms respectively. Some coordinates under these circumstances have the same values reducing the volume of calculations to a degree.

For the argon–fullerene interaction, the coordinates of the carbon atoms are fixed and distances between argon and carbon atoms are determined by the position of the approaching argon atom. The Lennard-Jones parameters for argon–argon and helium–helium interactions were taken here as $\varepsilon = 0.1654 \cdot 10^{-20}$ J, $\sigma = 0.3406$ nm and $\varepsilon = 0.01411 \cdot 10^{-20}$ J, $\sigma = 0.2556$ nm (Moore and Spencer 2001) and the corresponding values of parameters for the argon–carbon $\varepsilon = 0.10813 \cdot 10^{-20}$ J, $\sigma = 0.3380$ nm and for helium–carbon $\varepsilon = 0.03158 \cdot 10^{-20}$ J, $\sigma = 0.02955$ nm interactions have been calculated using the Lorentz-Berthelot combining rules.

## 3 Results and discussion

### 3.1 Direct calculation of the fullerene–fullerene potential

The interaction potentials between two $C_{60}$ fullerenes molecules calculated by this direct summation method for the two orientations of approach (hexagon–hexagon and pentagon–pentagon) differ noticeably from each other which represents about 6% in the region of the potential well. Additionally the potential well for the hexagon–hexagon case is located slightly closer to the centre of the fullerene molecule as seen in Fig. 1 and Table 1, where the average values of parameters for these cases also are presented.

In addition, during the pentagon–pentagon approach, we have examined the impact of mutual rotation of fullerenes about a common axis. In this case the rotation by an 36° angle does not practically change the position and depth of potential well.

**Table 1** Interaction potential parameters from direct calculations and predicted by (3) and (5)

| System | Direct calculations | | | Results of fitting | | |
|---|---|---|---|---|---|---|
| | $\sigma$, nm | $z_m$, nm | $\varepsilon \cdot 10^{+20}$, J | $\sigma$, nm | $z_m$, nm | $\varepsilon \cdot 10^{+20}$, J |
| C–C | 0.33540 | 0.37647 | −0.07069 | | | |
| He–C | 0.29550 | 0.33169 | −0.03158 | | | |
| Ar–C | 0.33800 | 0.37939 | −0.10813 | | | |
| He–$C_{60}$, pentagon | 0.59492 | 0.63559 | −0.25228 | 0.59500 | 0.63560 | −0.25225 |
| Ar–$C_{60}$, pentagon | 0.63699 | 0.68254 | −0.98632 | 0.63701 | 0.68316 | −0.98209 |
| $C_{60}$–$C_{60}$, pentagon | 0.95335 | 0.99880 | −6.55622 | 0.95337 | 0.99889 | −6.56494 |
| $C_{60}$–$C_{60}$, hexagon | 0.94822 | 0.99432 | −6.94723 | 0.94821 | 0.99428 | −6.94311 |
| $C_{60}$–$C_{60}$, average | 0.95079 | 0.99656 | −6.75173 | 0.95079 | 0.99658 | −6.75402 |

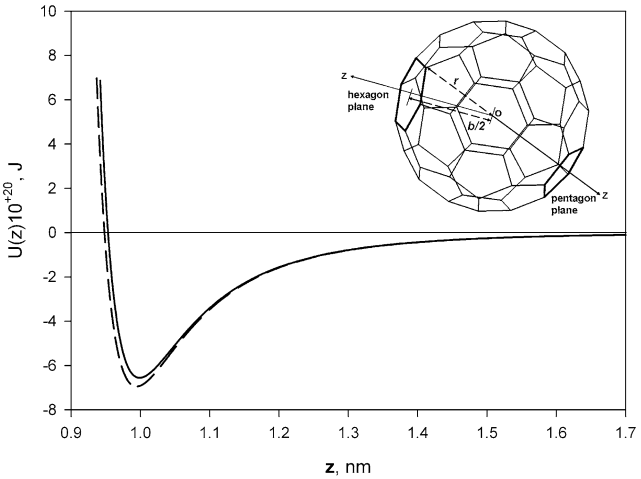


**Fig. 1** Interaction potentials between two $C_{60}$ molecules. Direct calculations for pentagon-pentagon (*solid curve*) and hexagon–hexagon (*dashed curve*) orientation

### 3.2 Derivation of the analytic equation for fullerene–fullerene interaction potential

It is very clear that the Lennard-Jones or Buckingham type of potential equation is unsuitable for the description an interaction between fullerenes themselves because they do not contain strongly repulsive cores. For fullerenes, the interaction potential tends to the infinite limit when centre to centre distance equals the diameter of fullerene instead of zero, as occurs for simple atoms. Therefore, it may be expected that a Kihara (1953) type of equation is more appropriate. However, taking into consideration that the carbon atoms in fullerenes have a two-dimensional arrangement, the exponents in the known Kihara (6-12) equation must be reduced by two units. By this means we have proposed here the following equation for the interaction potential between two fullerene molecules:

$$U(z) = \varepsilon \sqrt[3]{\frac{5^5}{3^3 2^2}} \left[ \left( \frac{\sigma - b}{z - b} \right)^{10} - \left( \frac{\sigma - b}{z - b} \right)^{4} \right] \tag{3}$$

or

$$U(z) = \varepsilon \left[ \frac{2}{3} \left( \frac{z_m - b}{z - b} \right)^{10} - \frac{5}{3} \left( \frac{z_m - b}{z - b} \right)^{4} \right] \tag{3a}$$

where the parameters $\varepsilon$ and $\sigma$ have their usual meanings, and $z_m$ is the position of the energy minimum of two approaching fullerene molecules and $b$ represents the closest distance of approach of the centres of the two fullerenes i.e. the inaccessible core diameter. The values of this latter distance, which depends on the orientation of fullerenes, lie in the range

$$2(r - \Delta) \le b \le 2r$$

where $r$ is the radius of a fullerene and $\Delta$ is the distance from the hexagon (or pentagon) plane to the surface of the fullerene sphere. These quantities are related by the following expression:

$$z_m = (\sigma - b) \sqrt[6]{\frac{5}{2}} + b \tag{4}$$

As seen from Fig. 2, the fit of the directly calculated potential points using (2) gives excellent results with the solid line predicted by these analytical equations (3) or (3a).

Here three parameters—$\varepsilon, b$ and $\sigma$ (or $z_m$) were employed. The mean-root-square error in the range depicted in Fig. 2 does not exceed 1%. Equally satisfactory results can also be obtained, if the quantity $b$ is replaced by distance $l$, where $l$ is the spacing between the centre of the fullerene and the plane of the hexagon (or pentagon) and only two parameters are then used. Thus, for a pentagonal plane $l = 0.67224$ nm and the fitted parameter $b$ equals 0.67777 nm, i.e. the difference is 0.8%.

### 3.3 Argon–fullerene potential

The interaction potential between a $C_{60}$ fullerene and argon as a test-atom have been calculated for the case when an argon atom is approaching the centre of a pentagon along

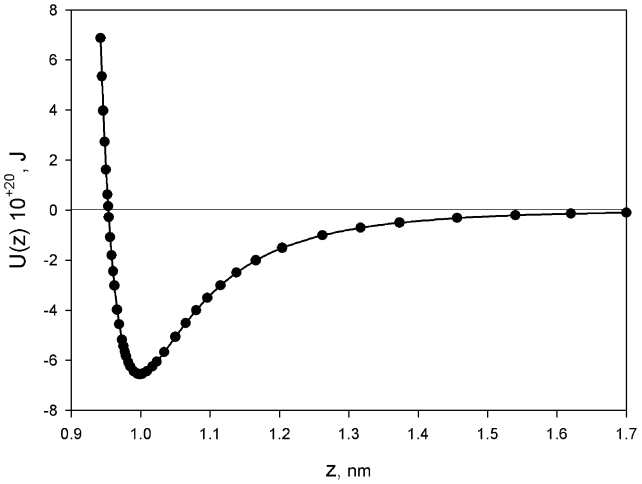


**Fig. 2** The result of the fit of the $C_{60}$–$C_{60}$ interaction potential from (3) (*solid curve*) with the calculated data from the direct summation method (*solid circles*)

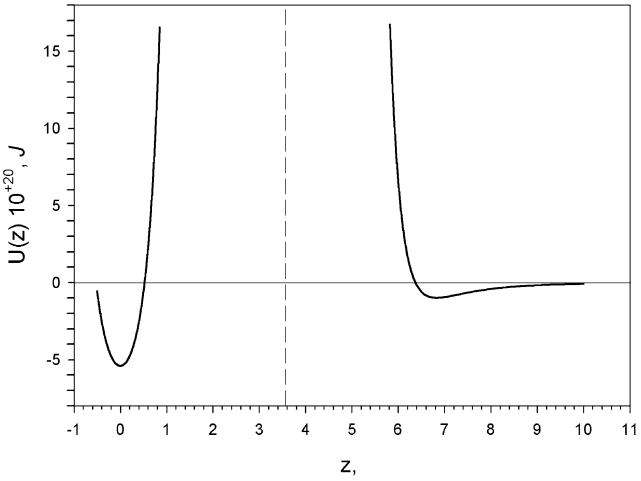


**Fig. 3** Interaction potential between argon atom and $C_{60}$–inside (*left curve*) and outside (*right curve*) of fullerene

a straight line passing through the origin of a coordinate system, which is placed at centre of fullerene. Although the space inside of fullerene is inaccessible for argon penetration (the potential energy barriers reach magnitudes of $3.5414 \cdot 10^{-15}$ J, i.e. the barrier is five orders of magnitude greater than the depth of the potential well), the corresponding interaction potential also may be calculated. The complete picture of the potential behaviour is presented in Fig. 3. It can be seen from Fig. 3 that the minimum of potential energy inside of fullerene is almost 5.5 times greater than the external minimum. Interestingly the minimum potential energy probed by Ar–$C_{60}$ inside fullerene constitutes about 83% of the minimum potential energy $C_{60}$–$C_{60}$ interaction, whereas the outer minimum is only 15%, as can be seen from Fig. 4 and also Table 1.

For a description of the outer part of the potential curve we propose the following expression:

$$U(z) = 4\varepsilon \left[ \left( \frac{\sigma - b}{z - b} \right)^{10} - \left( \frac{\sigma - b}{z - b} \right)^{5} \right] \tag{5}$$

or

$$U(z) = \varepsilon \left[ \left( \frac{z_m - b}{z - b} \right)^{10} - 2 \left( \frac{z_m - b}{z - b} \right)^{5} \right] \tag{5a}$$

The relation between the parameters of (5) and (5a) is given by following expression

$$z_m = (\sigma - b)\sqrt[5]{2} + b \tag{6}$$

The distinction between these expressions and the Kichara potential is the exponents, that is, (5-10) rather than (6-12) for the latter. Reducing of the exponents in the new equation is a direct consequence of the two-dimensional topological

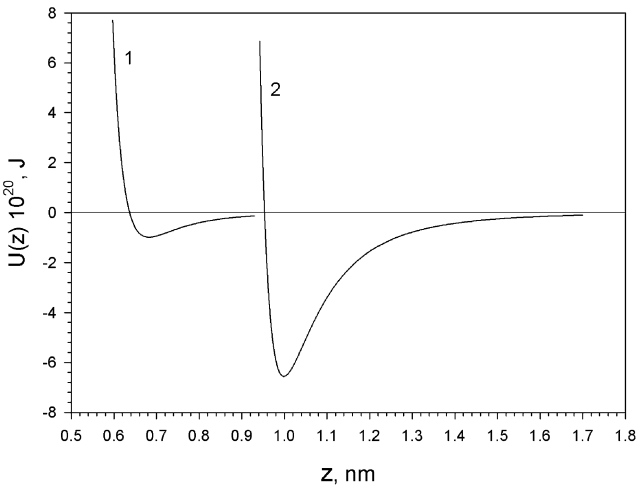


**Fig. 4** Comparison the potential functions of Ar–$C_{60}$ (curve 1) and $C_{60}$–$C_{60}$ (curve 2) interactions

arrangement of carbon atoms for one of interacting species, namely, the fullerene.

The argon–fullerene potential curve described by (5) is shown in Fig. 5 together with data points corresponding to the direct calculation of the argon–fullerene interaction potential. Here the high degree of fit between the proposed equation and the calculated data points may be readily seen.

### 3.4 Adsorption characteristics

Utilizing the Henry constant equation for a monoatomic adsorbate as given by

$$K_H = \int_0^\infty \left[ \exp\{-U(z)/k_B T\} - 1 \right] dz \tag{7}$$

where $k_B$ is the Boltzmann's constant and $T$ is the temperature, we were able to estimate the Henry constant for the

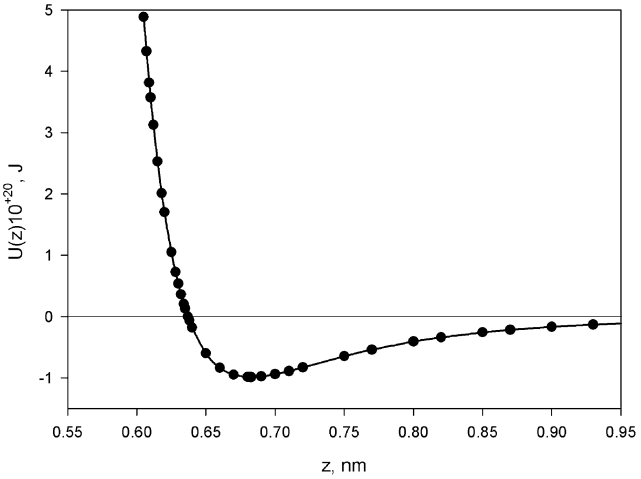


**Fig. 5** The result of the fit of the outer Ar–$C_{60}$ interaction potential by (5) (*solid curve*) with the calculated data from the direct summation method (*solid circles*)

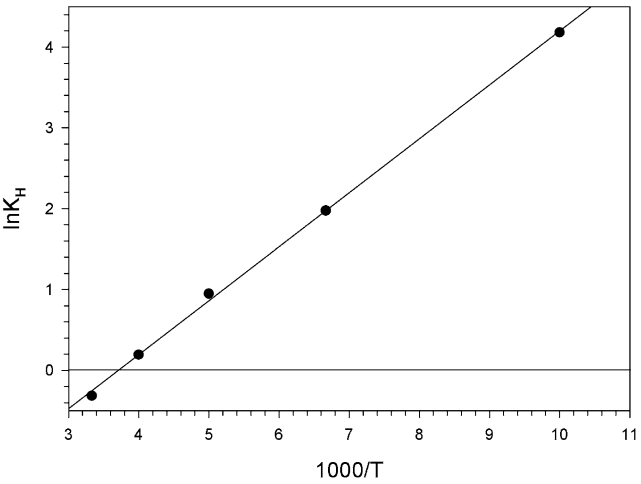


**Fig. 6** Dependence the Henry constants on temperature for the argon–$C_{60}$ fullerene adsorption system

argon–$C_{60}$ fullerene system at different temperatures. These results are shown in Fig. 6. The temperature dependence of the Henry constant then allowed evaluation of the initial isosteric heat of adsorption according to the expression:

$$q_0^{st} = -R\left(\frac{\partial \ln p}{\partial T^{-1}}\right)_{\Gamma} = R\frac{d\ln K_H}{dT^{-1}} \tag{8}$$

For the initial isosteric heat of adsorption we obtained $q_0^{st} = 5.552$ kJ/mol. For comparison, some related characteristic values are 5.714 kJ/mol for the argon–single-walled carbon nanotube ($r = 0.475$ nm) system (Mainwaring et al. 2005) and 9.755 kJ/mol for the argon–graphitised carbon black system (Constrabaris and Halsey 1957).

In addition, the interaction potential between a $C_{60}$ fullerene molecule and a helium atom has also been calculated. Using the calculated data, the temperature dependence

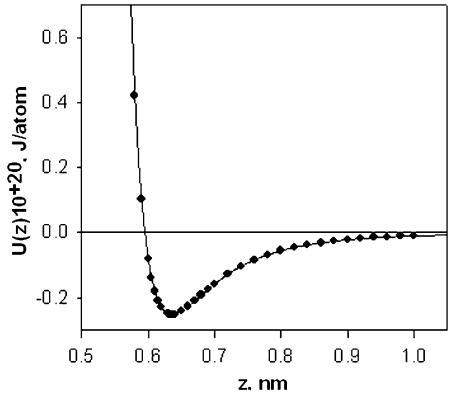


**Fig. 7** Interaction potential between helium atom and $C_{60}$ fullerene

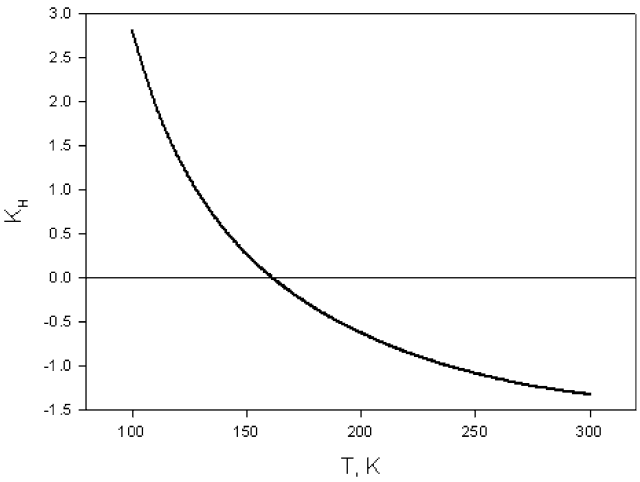


**Fig. 8** Dependence the Henry constants on temperature for the helium–$C_{60}$ fullerene adsorption system

of the Henry constant was also been estimated. For this system as shown in Figs. 7 and 8, results deserve attention because helium is widely used for calibration in the case of volumetric method of adsorption at room temperature. Our calculations show that the Henry constant for excess adsorption equals zero at 161 ± 1 K. This indicates that at room temperature excess adsorption is negative and the calibration misrepresents a true accessible volume for the adsorptive due to its underestimation. Notably, the result depends on the Lennard-Jones interaction parameters employed here (Gray and Gubbins 1984); whereas if we employ the parameters used, for instance, by Girifalco (1992) we obtain an even lower temperature for the point at which the Henry constant is zero. Although the error that arises from this negative adsorption when employing temperatures higher than that at zero excess adsorption is not unduly significant, it is not negligible.

## 4 Conclusions

We have presented a methodology for direct calculations of the potential energy of dispersion interactions between two $C_{60}$ fullerene molecules, as well as the argon and $C_{60}$ system, over a wide range of distances. New equations have been proposed for the analytical description of these potential energy interactions. These equations combine reasonable simplicity with high accuracy of description by relating the exponents to the topology of the systems. The calculated data and our proposed equation have been used for the determination of the Henry constants and the initial isosteric heat of adsorption for argon on fullerene.

## Nomenclature

- $b$ Distance associated with the strongly inaccessible cores of molecules (nm)
- $i, j, k$ Integer numbers
- $k_B$ Boltzmann constant ( $= 1.3806505 \cdot 10^{-23}$ J K$^{-1}$)
- $K_H$ Henry constant (nm)
- $l$ Twice spacing between the centre of the fullerene and the plane of the hexagon (or pentagon) (nm)
- $P$ Equilibrium pressure (Pa)
- $q_0^{st}$ Initial isosteric heat of adsorption (kJ/mol)
- $R$ Universal gas constant ( $= 8,314472$ J K$^{-1}$ mol$^{-1}$)
- $R_{ij}$ Current distance between $i$-th and $j$-th carbon atoms of two $C_{60}$ molecules (nm)
- $r$ Radius of a $C_{60}$ fullerene ( $= 0.3583$ nm)
- $T$ Temperature (K)
- $U$ Potential energy of interaction (J)
- $z_k$ Current distance between the centres of two $C_{60}$ molecules (nm)
- $z_m$ Distance between the centres of two interacting molecules at minimum potential energy (nm)
- $z_0$ Initial distance between the centres of two $C_{60}$ molecules (nm)

Greek Letters

- $\Gamma$ Adsorption excess in mass units (g)
- $\Delta$ Distance from the hexagon (or pentagon) plane to the fullerene sphere (nm)
- $\varepsilon$ Depth of the potential well (J)
- $\sigma$ Zero potential distance (nm)

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