Note on the Free Energy of Transfer of Fullerene C_{60} Simulated by Using Classical Potentials

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Diverse atomistic parameters of C_{60} have been developed and utilized to simulate fullerene solutions in biological environments. However, no thermodynamic assessment and validation of these parameters have been so far realized. Here, we employ extensive molecular dynamics simulations with the thermodynamic integration method in the isothermal−isobaric ensemble to investigate the transfer of a single fullerene C_{60} between different solvent environments using different potential models. A detailed analysis is performed on the structure and standard Gibbs free energy of transfer of C_{60} from benzene to ethanol. All of the interactions concerned in the transfer process are included via atomistic models. We notice that having only structural and dynamical properties is not decisive to validate reliable atomic parameters capable of describing a more realistic thermodynamic process. Thus, we employ the calculated free energy of transfer to validate more accurate atomic parameters for the solvation thermodynamics of fullerenes by direct comparison with the solubility experimental data.

The solubility of fullerene C_{60} in neat liquids and mixtures[1−4] has recently attracted an interdisciplinary interest due to the various emerging applications in biomedical technologies,[5−7] photosensitizers,[8] optoelectronic devices,[9] and the synthesis of fullerene-based nanomaterials.[10] As a fundamental interest, the medium plays a key role in the understanding of the interaction between C_{60} and the environment.[1,11] From the theoretical viewpoint, to explain the underlying causes of the fullerene solvation, a microscopic model of the interactions between the solute and solvent is required. Furthermore, thermodynamic conditions are necessary for a more realistic description of the solvated system under ambient conditions.[12] These requirements imply the use of appropriate computational simulations to obtain accurate and reliable properties of solutions containing dispersed nanoparticles. This has been the focus of our recent investigations on the solvated fullerene.[12−14]

Another useful factor regarding the solvation structures and dynamics of bare C_{60} is related to its geometric features, that is, the molecular surface area and the molecular volume.[15] Considering these aspects, the formation of a large nonpolar spherical solute may lead to significant hydrophobic effects.[7,16] Indeed, the dissolution of such a solute implies the disruption of many hydrogen bonding interactions in the bulk water, without forming new ones with the fullerene surface.[13] On the other hand, at this length scale, only a cavity solute model, as proposed by Chandler[17] for large nonpolar solutes, is not sufficient to describe fullerene aqueous solutions.[18] Despite the extremely low solubility of monomeric C_{60} in water,[1,2] the
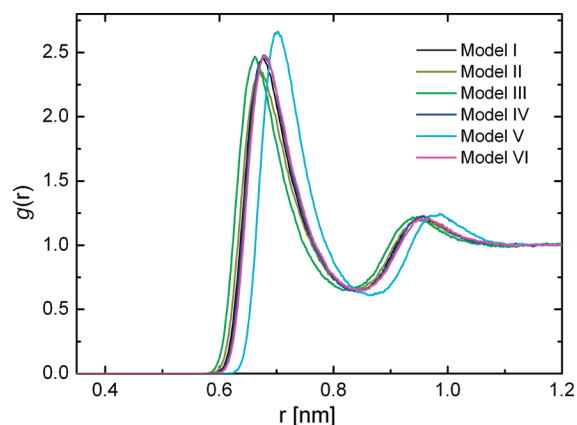

Figure 1. Calculated PDFs between the center-of-mass of C_{60} and water using different potential models. Models: I (ref 28), II (ref 27), III (ref 26), IV (ref 12), V (ref 29), VI (ref 24). A more detailed analysis of the profiles is given in Table S1 (Supporting Information).

attractive interactions between the solute and the solvent play an important role in stabilizing the fullerene aqueous solutions, which have intrigued experimentalists[19−22] and theoreticians[12,13,18,23,24] in the present decade.

As demonstrated by Marcus,[25] the solubility of C_{60} is dominated by the solvent polarizability. The knowledge that these molecules are nonpolar and interact by dispersion forces with surrounding molecules has led to the development of different atomistic potential models[12,24,26−29] for simulating the impact of fullerenes on the medium and vice versa. Usually, the solute−solvent interactions have been well described with

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TABLE 1: Position of the First Peak (in nm) and Number of Solvent Molecules in the PDF between the Centers-of-Mass of C_{60} and the Solvent Calculated with Different Potential Models

model [a]	water		ethanol		benzene	
	min	# solv	min	# solv	min	# solv
I	0.84	61	0.95	32	1.00	24
II	0.84	61	0.94	31	0.99	24
III	0.82	52	0.93	29	0.98	23
IV	0.84	61	0.95	32	0.99	24
V	0.86	66	0.97	34	1.02	25
VI	0.86	65	0.97	31	1.00	24

[a] I (ref 28); II (ref 27); III (ref 26); IV (ref 12); V (ref 29); VI (ref 24).

the pairwise Lennard-Jones (LJ) potential between the carbon atoms of C_{60} and the atoms (or united atoms) of the solvent (see Tables S1 and S2 in the Supporting Information). However, a critical assessment of the thermodynamic properties of fullerene solutions predicted by using these potential models is still lacking.[7] Although the room-temperature solubility of pure C_{60} has been determined experimentally in a wide variety of solvents,[1,2] the free energy of transporting a single C_{60} molecule between different solvent environments has not yet been determined theoretically[30] in order to ensure the accuracy and reliability of the interaction potentials by direct comparison with the experimental data.

In this Letter, we employ extensive atomistic molecular dynamics (MD) simulations (see Supporting Information for details) to show that small changes in the LJ parameters can lead to little different structural features of fullerene solutions but do lead to important differences in the Gibbs free energy of transfer of C_{60} between different solvents. We examine the dynamical aspects of the fullerene in both aqueous and organic solutions as well as the calculated free energy of transfer from benzene to ethanol under ambient conditions using six sets of all-atom LJ potentials (I–VI).[12,24,26–29] Thus, a prerequisite for using atomistic simulations as a predictive tool in this field will be the availability of validated potential models. To address the computational validation of a variety of potentials, we propose using systematic MD simulations combined with the thermodynamic integration algorithm (see Tables S3 and S4 in the Supporting Information) to obtain the solvation free energy of the fullerene in appropriate solvents.

First, we calculate and compare the structure of water around the fullerene solvation shells with the above-listed potentials (I–IV). In Figure 1, we display the pairwise radial distribution functions (PDFs) of the hydrated C_{60} using the different sets of

LJ parameters. In general, the PDFs present similar patterns, giving about 60 water molecules around the first solvation shell of C_{60} calculated via spherical integration.[31] The smallest value (~52 water molecules) is obtained using the parameters proposed by Qiao and Aluru.[26] A larger discrepancy in the number of solvent molecules is obtained within the second solvation shell. In this case, the parameters developed by Hotta et al.[27] and by Weiss et al.[24] give, respectively, ~116 and ~115 water molecules, whereas the remainder yields about 160. Notwithstanding, this discrepancy may be attributed to the somewhat imprecise definition of the second minimum at the PDFs, as seen in Figure 1. A more detailed analysis of the PDFs is presented in Table S5 (Supporting Information).

It is known that the solubility of fullerene is high in hydrocarbons and moderately low in polar organic solvents.[1,2] Thus, our next step is to analyze the performance of the aforementioned potential models to obtain the structural properties in these kinds of solvents. We have chosen ethanol, an important polar organic solvent for fullerene,[14,32] and benzene, which is employed in the Krätschmer−Huffman technique[33] of preparing and isolating C_{60}. Our results show that these potentials do not yield an abrupt change in the number of solvent molecules around the first solvation shell of the fullerene in both solvents. As displayed in Table 1, we obtain about 30 molecules in the case of ethanol and about 24 molecules in the case of benzene. The respective PDFs are displayed in the Supporting Information (Figures S3 and S4).

As can be seen from the above analysis, the structural properties of the solvent around the solute are not decisive to choose an appropriate set of LJ parameters. In order to provide a piece of information on the dynamical aspects of the solutions, we also investigate the translational diffusivity of the solute in different solvents using the diverse interaction potentials. Here, we calculate the self-diffusion coefficient of C_{60} from the mean square displacement (MSD) in the linear time regime (Supporting Information). As expected, this property exhibits a large sensitivity with respect to the LJ parameters[34] (see Table 2). For example, the parametrization of Girifalco,[28] which is close to the model adopted by Weiss et al.,[24] gives a diffusion constant in water of 1.27×10^{-5} cm^2 s^{-1}, while the latter gives 0.82×10^{-5} cm^2 s^{-1}.

Comparing the results for the diffusion constants of C_{60} in ethanol and that in benzene calculated with the different potential models, given in Table 2, we also note a large discrepancy. However, it is worth mentioning that experimental results of diffusion constants of C_{60} in benzene are rather dissonant.[35,36] The experiments give values of 0.83×10^{-5} and 2.38×10^{-5} cm^2 s^{-1}, whereas our calculated values vary from 0.07×10^{-5}

TABLE 2: Calculated Densities (ρ)[a] and Diffusion Constants (D) of the Fullerene Solutions using Different Potential Models (I–VI)

	I	II	III	IV	V	VI
			water			
ρ (kg m^{-3})	995.6	994.2	996.4	994.2	992.4	993.8
D (10^{-5} cm^2 s^{-1})	1.27 ± 0.06	0.85 ± 0.10	1.02 ± 0.14	0.89 ± 0.11	1.15 ± 0.09	0.82 ± 0.05
			ethanol			
ρ (kg m^{-3})	818.2	819.8	819.3	817.8	818.2	820.1
D (10^{-5} cm^2 s^{-1})	0.17 ± 0.14	0.25 ± 0.05	0.44 ± 0.29	0.66 ± 0.38	0.24 ± 0.08	0.18 ± 0.08
			benzene[b]			
ρ (kg m^{-3})	872.9	873.4	874.4	873.6	853.7	838.1
D (10^{-5} cm^2 s^{-1})	1.29 ± 0.81	1.44 ± 0.09	0.29 ± 0.14	0.45 ± 0.25	0.07 ± 0.15	0.41 ± 0.22

[a] Error estimates in the densities are of ±0.7 kg m^{-3}. [b] Experimental values of the diffusion constants in benzene are 0.83×10^{-5} (ref 35) and 2.38×10^{-5} cm^2 s^{-1} (ref 36).

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TABLE 3: Calculated Standard Gibbs Free Energy of Transfer (in kJ mol^{-1})^a of C$_{60}$ from Benzene to Ethanol with the Different Sets of LJ Potentials in Comparison with Experimental Data

	I	II	III	IV	V	VI	Expt.
$\Delta_{trn}G^0$	16.89	16.08	17.99	22.64	41.58	18.23	19.08;^{b} 22.91^c

^{a} Error estimates in the calculated free energies are in the range of 0.09 and 0.12 kJ mol^{-1} (see Table S4, Supporting Information). ^{b} Reference 1. ^{c} Reference 2.

cm^2 s^{-1}, with the model of Walther et al.,[29] to 1.44 × 10^{-5} cm^2 s^{-1}, with the model of Hotta et al.[27] As is well know, self-diffusion coefficients calculated via MD simulation depend significantly on the potential type and system size.[34] Therefore, the calculated diffusion constant of C$_{60}$ appears to be not adequate to validate a suitable set of LJ parameters.

Alternatively, to assess a number of potential models, we propose using the standard Gibbs free energy of transfer ($\Delta_{trn}G^0$) of the fullerene from a reference organic solvent (e.g., benzene) to a polar organic solvent (e.g., ethanol). At room temperatures, the transfer of a single fullerene from benzene to ethanol involves a measurable increase in $\Delta_{trn}G^0$. The corresponding enthalpy and entropy changes will be negative quantities in this process.[37] Thus, it is possible to assess these potential models in light of high-quality solubility data of C$_{60}$ in different species of solvents[1,2] at ambient conditions. We present the calculated values of $\Delta_{trn}G^0$ in comparison with the experimental data in Table 3.

Now, we note that the different sets of interaction potentials lead to significant differences in the transfer free energy. The LJ parameters developed by Qiao and Aluru[26] and Weiss et al.[24] give values of approximately 18 kJ mol^{-1}, which are close to the solvation free energy obtained by Ruoff et al.[1] (see Table 3). On the other hand, the potentials developed by Girifalco[28] and Hotta et al.[27] give values of approximately 17 and 16 kJ mol^{-1} that are, respectively, 2 and 3 kJ mol^{-1} below the measurements of Ruoff et al.[1] Considering the six sets of LJ parameters investigated here, the one derived by Walther et al.[29] gives an extremely high value of $\Delta_{trn}G^0$, that is, 41.58 kJ/mol, compared to the experimental data. Among these, the potential model proposed by Rivelino et al.[12] gives a free energy of transfer of 22.64 kJ/mol, which is in close agreement to the more recent solubility data from Marcus et al.[2] and is 3 kJ mol^{-1} above the data from Ruoff et al.,[1] as shown in Table 3.

In summary, we have examined carefully six sets of atomistic potential models (I−VI) for C$_{60}$ that are commonly employed in the literature to investigate structural and dynamical properties of fullerene solutions. We find that small changes in the LJ parameters may lead to similar patterns in the structural features of fullerene solutions; however, they can lead to important differences in the solvation free energy of fullerene C$_{60}$. In this way, we have simulated the Gibbs free energy of transfer of this solute from benzene to ethanol, considering ideal dilute solutions. Until now, no thermodynamic model taking into account explicit solvent molecules had been employed to explain the solubility of C$_{60}$. On the basis of the high-quality thermodynamic measurements in hundreds of solvents, we have used the solvation energies of C$_{60}$ comprehensively to validate a set of atomic parameters by direct comparison with experimental data. Finally, our study allows a careful assessment of the LJ parameters that are currently being used in computer simulations of fullerene transport in biological systems.

Supporting Information Available: Computational details, parameters of the potential models, and dynamics and structural analysis of the fullerene solutions. This material is available free of charge via the Internet at http://pubs.acs.org.

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