Free-energy coarse-grained potential for C60

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Free-energy coarse-grained potential for C₆₀

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We propose a new deformable free energy method for generating a free-energy coarse-graining potential for C₆₀. Potentials generated from this approach exhibit a strong temperature dependence and produce excellent agreement with benchmark fully atomistic molecular dynamics simulations. Parameter sets for analytical fits to this potential are provided at four different temperatures. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4932591>]

I. INTRODUCTION

C₆₀, discovered in 1985,¹ has the structure of a truncated icosahedron, with 12 pentagonal faces, 20 hexagonal faces, and 60 vertices for 60 carbons. This molecule was named Buckminsterfullerene, often shortened to “buckyballs,” after the American architect Buckminster Fuller, who designed geodesic domes with similar structures in the 1960s. While C₆₀ has not seen wide success in terms of applications, it has played a role in fundamental studies, and suggestions for applications, for example, as a vehicle for drug delivery,² continue to be advanced.

Recently, considerable attention has been directed towards the development of coarse-graining (CG) methodologies for molecular dynamics (MD) simulations of materials.^{3–12} Buckyballs are useful in this context as a prototypical molecule for the development and testing of CG techniques. There are two reasons for this. First, there is no ambiguity over where to place the CG site for each C₆₀ molecule, since the molecule has such high symmetry, and the center of mass (COM) is clearly the correct choice. Second, each molecule contains only 60 atoms, which makes performing fully atomistic MD simulations as a basis for comparison computationally inexpensive.

In this work, we first review the Girifalco potential,^{13,14} a commonly used CG pair potential for C₆₀.^{15–17} We then present a new method for dynamic generation of a CG potential from MD simulations, which we call the *deformable free energy potential*. This method is applied to a pair of C₆₀ molecules at $T = 0$ and at finite temperature. The potentials generated by the deformable free energy method represent the CG free energy, not the CG internal energy, and thus exhibit a strong dependence on temperature but produce superior agreement with fully atomistic molecular dynamics simulations. We provide analytical fits to these potentials, together with relevant constants for further research.

The Girifalco potential, augmented with vibrational free-energy corrections, has already been shown to be effective in the simulation of crystalline fcc C₆₀.^{13,14} We believe our potential will be most effective for the simulation of C₆₀ in the gaseous and liquid phases.

The Girifalco potential was derived by treating each C₆₀ molecule as a sphere, with a uniform density of carbon atoms “smeared out” across the surface. Girifalco assumed that the carbon atoms interact through a Lennard-Jones potential,¹⁸

$$V_{\text{LJ}}(x) = -\frac{A}{x^6} + \frac{B}{x^{12}}, \quad (1)$$

where x is the separation of the atoms and $A = 0.001\,926\,6$ kJ/mol (nm)⁶ and $B = 3.357\,787 \times 10^{-6}$ kJ/mol (nm)¹². The interaction energy between the C₆₀ molecules may then be evaluated analytically by integrating over the surfaces of the two spheres. The resulting effective pair potential is given by

$$V(r) = -\alpha \left[\frac{1}{s(s-1)^3} + \frac{1}{s(s+1)^3} - \frac{2}{s^4} \right] + \gamma \left[\frac{1}{s(s-1)^9} + \frac{1}{s(s+1)^9} - \frac{2}{s^{10}} \right], \quad (2)$$

where r is the COM separation between C₆₀ molecules, $s = r/2a$, $2a = 0.71$ nm is the C₆₀ diameter, $\alpha = N^2 A/12(2a)^6$, $\gamma = N^2 B/90(2a)^{12}$, $N = 60$, and A and B are as above. A and B were obtained by computing the energy of the fcc C₆₀ crystal and matching the results to data for the heat of sublimation and the lattice constant.

II. METHOD

A. Simulation parameters

In this work, the Optimized Potentials for Liquid Simulations All-Atom (OPLS-AA)¹⁹ force field was used for all atomistic simulations. This force field includes short-ranged bonding terms acting only between atoms on the same molecule, as well as a long-ranged inter-atomic van der Waals interaction acting between atoms on different molecules. This force field was also used to define the atomistic physical system to be modeled with the CG force field: we consider a CG force field accurate if it yields results that match those produced by the atomistic OPLS-AA force field. The GROMACS 4.5.5²⁰ software package was used for all MD simulations, both atomistic and coarse-grained.

A cutoff radius of 1.1 nm was used for the non-bonded interactions, with a neighbor list cutoff length of 1.2 nm. A Langevin thermostat²¹ with a time constant of 2 ps was used during an initial 100 ps NVT simulation to bring the system to

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the target temperature. The thermostat was then switched off, and all statistics were gathered from a 1 ns NVE simulation with no thermostat applied.

The CG simulations were performed by supplying our CG potentials to GROMACS as tabulated files on a 0.0005 nm grid suitable for double precision calculations. The same parameters were used as in the fully atomistic simulations, except that the cutoff radius and neighbor-list cutoff were increased to 1.8 nm and 1.9 nm, respectively. This is because the tabulated potential refers to interactions between *molecules* rather than individual carbon atoms, so the diameter of a single C₆₀ molecule (0.70 nm) must be added to the cutoff radius to ensure that we still account for the correct number of interactions between carbon atoms.

B. Generating a rigid $T = 0$ potential

We first generated a CG potential at $T = 0$ using the method of Girifalco. We refer to our CG potential generated in this manner as the *rigid $T = 0$ potential*, since the C₆₀ molecules are treated as rigid spheres with no intramolecular deformation present. In order to make a fair comparison with our later CG potentials generated using the OPLS-AA force field, it is necessary to calculate the radius a of an isolated molecule at $T = 0$, using the OPLS-AA Lennard-Jones parameters for carbon. These parameters are $A = 0.002\,344\,9$ kJ/mol (nm)⁶ and $B = 4.693\,426 \times 10^{-6}$ kJ/mol (nm)¹², which differ significantly from the fitted values used by Girifalco (see Introduction). To obtain this radius a , we performed a steepest descent energy minimization of the atomic positions in a single molecule, until the maximum force on any atom was less than 0.0005 kJ/mol nm⁻¹. We then calculated the mean distance of each carbon atom from the C₆₀ COM, yielding $2a = 0.70$ nm.

C. Generating a deformable free energy potential at $T \geq 0$

We now describe our new method for generating a CG potential for C₆₀, which we have called the *deformable free energy potential* since the C₆₀ molecules are now allowed to deform according to the properties of the underlying OPLS-AA force field.

First, we perform a fully atomistic MD simulation of two C₆₀ molecules, held at a fixed COM separation. The COM separation was kept fixed to within 1 part in 10⁹ using the SHAKE constraint algorithm (Fig. 1). This simulation consists

FIG. 1. Two C₆₀ molecules constrained at a COM separation of 0.9 nm.

of 20 ps of NVT thermalization, followed by 20 ps under the NVE ensemble with the thermostat switched off. During the NVE run, the mean force between the C₆₀ COMs is calculated. We repeat this procedure 100 times, each time using a random initial configuration and orientation of the two molecules. This procedure is repeated for each COM separation r between 0.9 nm and 2.0 nm in 0.025 nm increments, to yield the force as a function of distance $f(r)$. We perform a weighted cubic spline fit to this data to obtain a smooth force, using the standard error on each data point as a weight. The integral of this force provides a two-body approximation to the true many-body CG potential of mean force,³

$$V_{\text{CG}}(\mathbf{R}) = -k_B T \ln Z_{\text{CG}}(\mathbf{R}) + \text{const.} \quad (3)$$

Here, $\mathbf{R}$ is the set of N CG positions ($\mathbf{R}_1, \dots, \mathbf{R}_N$), k_B is Boltzmann's constant, T is the temperature, and Z_{CG} is the CG partition function. This is given by

$$Z_{\text{CG}}(\mathbf{R}) = \int d\mathbf{r} \exp[-V(\mathbf{r})/k_B T] \delta(\mathbf{M}(\mathbf{r}) - \mathbf{R}), \quad (4)$$

where $\mathbf{r}$ is the set of n atomistic coordinates ($\mathbf{r}_1, \dots, \mathbf{r}_n$), $V(\mathbf{r})$ is the atomistic potential energy function, δ is the Dirac delta function, and $\mathbf{M}$ is a CG mapping function which maps atomistic coordinates onto CG coordinates. For the special case of two C₆₀ molecules, the total number of atoms is $n = 120$, the number of coarse-grained coordinates is $N = 2$, and the two three-dimensional vectors that make up $\mathbf{M}(\mathbf{r})$ are the mean positions of the atoms belonging to the two molecules. The form for the CG potential given in Eq. (3) has the advantage that the thermodynamic expectation value of any quantity expressible purely as a function of the CG coordinates will be the same regardless of whether it is measured in the atomistic or CG ensemble.³

III. RESULTS AND DISCUSSION

The CG potentials generated using the methods described above are plotted for a range of temperatures in Fig. 2. The deformable free energy potential generated at 0K differs slightly from the rigid $T = 0$ potential. The minimum in the

FIG. 2. Our deformable CG potential generated at five different temperatures. Also shown is the rigid $T = 0$ potential calculated with our parameters. Note that the deformable 0 K potential is generated using the same method as the other four deformable potentials and not by relaxing the two C₆₀ molecules to their lowest energy configuration for a given COM spacing.

TABLE I. Coefficients used in Eq. (5) to obtain polynomial fit to the deformable free energy potentials at four different temperatures. The average RMS error of these fits is 0.32 kJ/mol.

n	100 K	300 K	1000 K	2500 K
6	-1.256×10^4	-9.039×10^4	-3.682×10^4	-4.332×10^4
7	8.936×10^4	6.338×10^5	2.776×10^5	3.28×10^5
8	-2.57×10^5	-1.833×10^6	-8.574×10^5	-1.018×10^6
9	3.8×10^5	2.798×10^6	1.388×10^6	1.657×10^6
10	-3.014×10^5	-2.374×10^6	-1.241×10^6	-1.491×10^6
11	1.189×10^5	1.061×10^6	5.804×10^5	7.027×10^5
12	-1.738×10^4	-1.947×10^5	-1.107×10^5	-1.353×10^5

rigid $T = 0$ potential is shifted slightly to the right, since the C_{60} molecules are not free to compress each other, which causes their equilibrium COMs to be kept further apart.

When generating the deformable free energy potentials, the molecules are free to deform according to the properties of the OPLS-AA force field as they approach each other. This is why our potential does not reduce to the rigid $T = 0$ potential at zero temperature. We have fitted an inverse power law function to the CG potentials shown in Fig. 2. The fitting function is of the form

$$V_{CG}(x) = \sum_{n=6}^{12} \frac{A_n}{x^n}. \quad (5)$$

The fitting coefficients A_n are given in Table I.

We then performed a sequence of fully atomistic MD simulations as a benchmark for comparing our CG potentials. These simulations consisted of 1000 C_{60} molecules under periodic boundary conditions. A time step of 1 fs with the velocity Verlet integrator was used throughout. Each simulation began with a 10 ps NVT thermalization using the Langevin thermostat, followed by a 100 ps NVE simulation with the thermostat switched off. Statistics were collected only during the NVE simulation. All other parameters were the same as in the constrained-pair simulations described above.

In Fig. 3, we have plotted the pressure of a system of 1000 C_{60} molecules as a function of density at a constant temperature of 2500 K. The density was controlled by modifying the periodic box dimensions, and the pressure was calculated from NVE simulation results only.

FIG. 3. Pressure of a system of 1000 C_{60} molecules as a function of density at 2500 K. Solid lines are spline fits as a guide to the eye.

FIG. 4. Pair correlation function for a system of 1000 C_{60} molecules at a temperature of 2500 K and a density of 700 amu/nm³.

Our free energy potential generated at 2500 K is able to reproduce the pressure found from atomistic simulations very accurately, whereas the rigid $T = 0$ potential fails. The precise depth of the potential well in the CG potential is significant for pressure calculations, since too deep a well causes the C_{60} molecules to spend more time on average trapped inside the well. This in turn causes the virial term used to calculate the pressure to decrease, which decreases the total pressure. The pair correlation function of a system of 1000 C_{60} molecules at a temperature of 2500 K and a density of 700 amu/nm³ is shown in Fig. 4. By calculating the pair correlation function at a range of densities, it is possible to calculate the mean coordination number of the molecules in a system of C_{60} as a function of density (Fig. 5). Conventionally, the coordination number is taken to be the integral of the radial distribution function (RDF) from zero to the position of the first minimum. Since we are varying the density, for consistency we have integrated to a fixed distance of 1.1 nm instead.

Our deformable free energy CG potential reproduces the fully atomistic result very well. This is because the potential well depth and position have been parameterized correctly to take account of temperature. However, the rigid $T = 0$ potential overestimates the coordination number, since the deeper potential well over-binds the C_{60} molecules. The over-binding causes the peak in the RDF at the position of the potential minimum to be more pronounced than in fully atomistic MD simulations.

FIG. 5. Coordination number of the molecules in a system of C_{60} as a function of density at 2500 K. Lines are a guide to the eye.

FIG. 6. Diffusion constant of C_{60} as a function of density at 2500 K.

In Fig. 6, we have plotted the self-diffusion constant of a system of C_{60} molecules as a function of density at a temperature of 2500 K. Statistics from the NVE simulations only were used. In this case, both CG potentials are in close agreement with the reference atomistic MD simulation results. From other work, we have found that the diffusion constant is relatively insensitive to the exact form of pair potential used to simulate C_{60} . This may be because the C_{60} molecules are essentially undergoing hard sphere diffusion.

IV. CONCLUSION

In this work, we have proposed a new method to generate a CG potential using simulations of constrained pairs of molecules, which we have called the deformable free energy potential. For the case of C_{60} molecules in the liquid/gas phases, we have shown that this potential provides close agreement with benchmark fully atomistic simulation results. It is clear from our simulation results that using a temperature-dependent CG force field is essential to describe the finite temperature properties of the system correctly.

Whilst the deformable free energy potential must be regenerated at each temperature, it has the advantage of being reasonably computationally inexpensive to obtain, since only several short MD simulations of a pair of constrained molecules are required. We found that CG simulations using the deformable free energy potentials were approximately 1200 times faster than the equivalent fully atomistic MD simulations of 1000 C_{60} molecules. In addition, because the high-frequency degrees of freedom have effectively been integrated out of the CG potential, it is possible to use a larger time step in the CG simulations to further enhance computational efficiency. We found that a time step of 3 fs could be used with negligible effect on energy conservation, although the CG simulation results given above all use a time step of 1 fs to maintain consistency with the atomistic simulations.

Existing force-matching methods for generating CG potentials often suffer from the problem of having to solve an extremely large system of linear equations in order to find optimal CG force field parameters. The deformable free energy

approach avoids this by a direct evaluation of the mean forces between CG sites. Force-matching methods also suffer from sampling problems at small intermolecular separations, due to short-range repulsion between the molecules. The deformable free energy approach does not have this issue, since the molecules are explicitly made to sample unfavorable regions of phase space by the constraint force.

The deformable free energy approach can readily be extended to other, more complex molecules. Any small, relatively rigid molecules which can be represented by a single CG site would be good candidates for this method. There is no requirement that the two molecular species be the same, so it is possible to generate inter-species CG potentials. It should also be possible to generalize the method to molecules represented by more than one CG site. This can be done by individually constraining CG sites on opposite molecules, whilst allowing the other degrees of freedom to follow their unconstrained dynamics. This generates a sequence of effective pair potentials, allowing us to build up an entire CG force field. This is currently the subject of further research.

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