Adhesion energy of ethane–graphite interface: Atomistic study

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Abstract. Adhesion energy is an important characteristic of interfacial interactions. Usually one apply notion of adhesion energy to solid–solid interfaces, but it also could be extended to gas–solid and liquid–solid interfaces. In latter case phenomenon of adsorption is closely related to the adhesion energy. In this work we apply molecular dynamics method to calculate the specific adhesion energy for gas and liquid ethane on a graphite substrate. Influence of temperature and density on the value of the specific adhesion energy is investigated. Langmuir adsorption model is applied to interpret results and establish connection between notions of adsorption heat and specific adhesion energy. Appearance of multilayer adsorption is detected for higher densities. Developed model and numerical approach to calculate adhesion energy and surface coverage can be applied for different types of the adsorbate and the substrate.

1. Introduction
Adhesion energy is the main characteristic of the interaction between the interfaces. This is the energy that is released when one surface comes into contact with another surface. Computational studies using atomistic calculations [1, 2] provide valuable insights into structure and energetic changes that occurs between surfaces. The procedure to calculate the energy of adhesion between two solid surfaces is straightforward. The basic idea is to measure potential energy between two surfaces at different distances with relaxation [3]. The algorithm of evaluation the adhesion energy of gas–solid and liquid–solid interface is more complicated. There are a number of different ways to obtain value of adhesion energy from atomistic calculations: (method 1) difference of energies between combined system (solid surface + gas or liquid) and two isolated systems, (method 2) calculate heat adsorption from interpretation of atomistic data [4, 5] using one of the adsorption isotherms such as Langmuir isotherm.

In the present work, we use both methods to calculate the adhesion energy between ethane and graphite and show that they give comparable results. Molecular dynamics (MD) method is used to obtain atomistic data. Langmuir adsorption isotherm is applied to establish connection between adsorption and adhesion. Proposed approach is applicable both to liquid–solid and gas–solid interfaces. In this study we consider only plain surface. It should be noted, that the roughness of the surface [6, 7] and confinement [8] can also contribute to adhesion energy.

2. Methods
Software package LAMMPS [9] (large-scale atomic-molecular massively parallel simulator) is used to perform MD simulations. Graphene layers are generated with the use of the VMD...
Table 1. Lennard-Jones potential parameters used in this work. Cut-off radius $r_{\text{cut}}$ for all cases in this study is 14 Å.

| LJ parameter | CH$_3$–CH$_3$ | C–CH$_3$ (I) | C–C (I) | C–CH$_3$ (II) | C–C (II) |
|--------------|----------------|-------------|---------|---------------|---------|
| $\sigma$, Å  | 3.750          | 3.575       | 3.400   | 3.575         | 3.400   |
| $\varepsilon$, meV | 8.450        | 4.900       | 2.840   | 4.510         | 2.410   |

Figure 1. Side view of MD simulation. The density is set equal to 0.166 g/cm$^3$. Temperature is 300 K. Formation of second layer can be seen.

software package [10]. The boundary condition is set to periodic in order to model continuous graphene crystal.

Lennard-Jones potential is used to estimate the energy of adhesion of ethane to a graphite substrate. The TraPPE (transferable potentials for phase equilibria) united atom [11] is used to describe ethane–ethane interaction. This coarse grain potential is more computationally efficient than full atomic potentials and it is known to describe thermodynamical properties with high level of accuracy [12]. This force field implies that CH$_3$ is pseudo-atom that makes calculations computationally efficient. The bond length between CH$_3$ sited is fixed and equal to 1.540 Å. For comparison we use two Lennard-Jones parameters for C–CH$_3$. Both are derived from Lorentz–Bertholot combining rules [13]. In first case we take C–C from Lennard-Jones part of AIREBO potential [14] (I), which is known to describe carbon materials properties well [15], in second case parameters are taken from study [16] (II). The calculations with second parameterization are performed only for 310 K to check sensitivity of adhesion energy to potential parameters. All parameters are shown in table 1.

For method 1 to calculate the adhesion energy, we simulate 3 cases: ethane–graphite system, only ethane system, only graphite system. To evaluate the adhesion energy we measure the potential energy per unit area difference between combined graphite–ethane system and separated systems. Thus the adhesion energy can be calculated as $\gamma_{SB} = (U_{\text{graphite+ethane}} - (U_{\text{graphite}} + U_{\text{ethane}}))/S$. Carbon atoms do not interact during simulations in this study, therefore we used $U_{\text{graphite}} = 0$ in this equation.

In graphite–ethane system 3 graphene layers represent substrate (figure 1), which is generated using VMD. The sizes of graphene layer are $L_x = 100.698$ Å and $L_y = 102.098$ Å, where $L_x, L_y$
are the lengths in \( x \) and \( y \) directions. The \( z \)-length of the simulation box is \( L_z = 107 \text{ Å} \), the substrate fills 6.7 Å, the remaining space is filled by ethane. Initially the ethane molecules are inserted into the simulation box in simple cubic lattice. Different initial densities are set to study pressure dependence of the adhesion energy, also we consider different temperatures. Then the ethane molecules are allowed to move in the \( NVT \) ensemble. The temperature is set to 280, 290, 300, 310 K to study ethane below and above critical temperature. The carbon atoms in graphite are fixed. After the energy of the system stabilizes, we assume that equilibrium is achieved, and statistical information can be gathered.

To simulate the ethane system, the separate calculations are performed. The number of ethane molecules is the same as in corresponding case of the graphite–ethane system. The size of the simulation box is \( L_x = 100.698 \text{ Å} \), \( L_y = 102.098 \text{ Å} \), \( L_z = 100 \text{ Å} \). Then ethane molecules are allowed to move in the \( NVT \) ensemble. The temperature is set to corresponding calculations of graphite–ethane system.

To apply method 2, one needs to obtain surface coverage of the graphite. To evaluate surface coverage we calculate averaged number density of ethane molecules near substrate in \( z \) direction. Example of this density distribution is shown in figure 2. Then we obtain the number of molecules in the first layer by integrating this function from 0 to the first minimum of density distribution.

To calculate pressure of ethane in case of graphite–ethane system, we select molecules located in the gap between \( z \) coordinates: 25 Å and 75 Å. Then the per-atom stress tensor is evaluated according to [17]. After averaging the per-atom stress tensor and obtaining the total stress tensor of the ethane atoms, the pressure is calculated as a minus trace of the obtained stress tensor.

### 3. Results and discussion

Langmuir adsorption model is used to evaluate specific adhesion energy according to method 2. We compare results of such prediction with direct MD calculation of adhesion energy. To apply Langmuir adsorption model we have to deal only with low densities because one of the basic assumptions is mono-layer coverage. Thus we select cases with only one layer adsorption, it is indicated by one maximum in figure 2. The pressure of ethane in this case is calculated using method described in previous section. Then we fit MD points to the Langmuir isotherm.
Table 2. Table of equilibrium constants $K$ for different temperatures.

| Temperature, K | 280 | 290 | 300 | 310 |
|---------------|-----|-----|-----|-----|
| $K$, 1/MPa    | 9.2 | 5.9 | 4.3 | 3.5 |

Figure 3. Surface coverage as a function of gas pressure at different temperatures: markers represent MD results; lines are Langmuir isotherm approximation.

\[ \theta = \rho / \rho_m = K_p / [1 + K_p], \]

where $\theta$ is the fractional occupancy of the adsorption sites; $\rho$ is the specific density per unit area; $\rho_m$—the specific density per unit area for the fully filled adsorption layer; $p$ is pressure of ethane gas under the adsorbed layer; $K$ is equilibrium constant of the reaction between the adsorbate molecule $A$ and an empty site $S$,

\[ A + S \leftrightarrow A_{ad}, \quad (1) \]

where $A_{ad}$ is an adsorbed complex.

We use the method of least squares to adjust parameters: equilibrium constant $K$ is adjusted for every temperature, density of the fully filled adsorption layer $\rho_m$ is the same for all cases because physical number of available sites are constant and depend only on the geometry and material of the substrate. We obtain $\rho_m = 4.3$ molecules/nm$^2$. Fitting equilibrium constants can be found in table 2. Plotted points of MD calculation of surface coverage and corresponding Langmuir isotherm are shown in figure 3.

The results given in table 2 allow to calculate the heat of adsorption $\Delta H$:

\[ K = K_0 e^{-\Delta H / kT}. \quad (2) \]

We take the log of both sides of 2 and fit the data using the method of least squares, which gives us $\Delta H = -0.242$ eV. Then we multiply the heat of adsorption by number of molecules in the adsorbed layer and divide it by area of surface to obtain the specific adhesion energy: $\gamma = -\Delta H N / S$. We take negative as we treat $\gamma$ as the gain in energy due to adsorption. On the other hand the specific adhesion energy is calculated directly from MD as energy difference between graphite–ethane and ethane systems. Both estimations are shown in figure 4. For low
Figure 4. Specific adhesion energy at different temperatures: solid lines are calculated directly from MD; dotted lines are evaluated from the Langmuir isotherm.

densities Langmuir model gives good match with direct MD calculations, while for high densities the assumption of mono-layer adsorption is not satisfied that is why the divergence is observed.

4. Conclusion

We perform MD simulations to calculate the surface coverage and the specific adhesion energy for different densities and temperatures of the graphite–ethane system. We use Langmuir adsorption model to interpret the results for low densities and predict from them the specific adhesion energy. One should use advanced adsorption models, such as Brunauer–Emmett–Teller theory, to get more precise estimation. Nevertheless, the benchmark shown in this work shows the possibility of prediction of specific adhesion energy from adsorption models.

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