Test-area surface tension calculation of the graphene-methane interface: Fluctuations and commensurability

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The surface tension (γ) of methane on a graphene monolayer is calculated by using the test-area approach. By using a united atom model to describe methane molecules, strong fluctuations of surface tension as a function of the surface area of the graphene are evidenced. In contrast with the liquid-vapor interfaces, the use of a larger cutoff does not fully erase the fluctuations in the surface tension. Counterintuitively, the description of methane and graphene from the Optimized Potentials for Liquid Simulations all-atom model and a flexible model, respectively, led to a lessening in the surface tension fluctuations. This result suggests that the origin of fluctuations in γ is due to a model-effect rather than size-effects. We show that the molecular origin of these fluctuations is the result of a commensurable organization between both graphene and methane. This commensurable structure can be avoided by describing methane and graphene from a flexible force field. Although differences in γ with respect to the model have been often reported, it is the first time that the model drastically affects the physics of a system. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4984577>]

I. INTRODUCTION

The interaction of fluid with solid interfaces is a key-factor for technologically important applications such as sensors, coatings, wetting, drying, and adhesion. Understanding this interaction opens the way of designing new nanofluidic devices that can offer alternative sustainable solutions for energy conversion, water filtration, and desalination.^{1–6} Controlling this interaction amounts to design surfaces with a given hydrophobicity or hydrophilicity that is relevant in biological applications (tissue integration) and in material sciences (self-cleaning surfaces). The wettability of a solid surface can be evaluated through the measurement of the contact angle which is given by Young-Dupre's basic relation⁷ $\cos \theta = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}}$ that relates the contact angle θ to the solid-liquid (γ_{SL}), solid-vapor (γ_{SV}), and liquid-vapor (γ_{LV}) interfacial tensions. The experimental determination of the contact angle depends on the impurities/defects on the surface that can lead to the scattering of the contact angle values for some solid-liquid interactions. For example, the experimental determination of the contact angle of water on a graphite surface was found to range from 30° to 80° under different experimental conditions.^{8–12} Since the surface of the material is critical for the compatibility with the surrounding environment, a number of molecular simulations have been performed to describe the interfacial region at the atomistic scale. Some of these atomistic simulations have been used to predict the contact angle of water on different surfaces.^{13–18} The molecular modeling considers the flat

and homogeneous surfaces. The value of the contact angle depends on the chemical nature of the surface, and other parameters such as the roughness and the chemical heterogeneity have been much less investigated from this theoretical approach.

Another way of estimating the solid-liquid interaction is to calculate the solid-liquid interfacial tension γ_{SL} . Whereas the calculation of the liquid-vapor and liquid-liquid interfacial tensions is now under control,¹⁹ the prediction of the solid-liquid interfacial tension by molecular simulations is much more challenging and as a result much less widespread.^{20–24} Indeed, the calculation of the interfacial tension from two-phase simulations has been applied to different liquid-vapour^{25–28} and liquid-liquid²⁹ planar interfaces through the mechanical^{30,31} and thermodynamical³² routes, and the dependencies of the surface tension on the temperature, pressure, and composition have been successfully reproduced by the two-phase simulations.³³

We propose here to apply the thermodynamics definition of the interfacial tension to predict the graphene-methane surface tension. Indeed, the graphene monolayer, which can be considered as the thinnest membranes, is a very interesting nanostructure for the development of nanofluidic devices.^{5,6,34} On the other hand, this system has often served as a model system for physical adsorption phenomena, while more recently, the study of methane adsorption on carbonaceous materials was motivated by the search for new storage systems for natural gas. To the best of our knowledge, only a few works have been reported on the surface tension calculation of fluids (gas or liquid) on the graphene monolayer,^{35,36} while this last decade numerous works have been devoted to the surface tension calculation of liquid-vapor interfaces with atomistic

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simulations.^{25–28,32,37} Thus, it has been shown that the surface tension was slightly sensitive to the surface area while γ was strongly affected by the models.¹⁹ Although the surface tension differs with respect to the model, interfacial physics was always well conserved. In this work, our objective is to investigate how the surface area and model affect the surface tension of a simple fluid, methane, interacting with a graphene monolayer. We do not aim to deeply investigate the microscopic structure of methane close to the graphene surface.

II. MODELS AND COMPUTATIONAL DETAILS

Graphene was kept rigid and described from the Lennard-Jones potential with parameters developed by Werder *et al.*¹³ In the case of a flexible graphene (FLEX model), we used the bonding, bending, and torsion potentials described in Ref. 38. Methane was modeled by using both the united atom (UA) model³⁹ and non-charged all atom (AA) description of the Optimized Potentials for Liquid Simulations (OPLS)^{40–42} model. Indeed, it was shown that a non-charged version of the OPLS-AA model⁴² was able to reproduce accurately the thermodynamics properties of the liquid-vapor equilibrium. The UA force field developed by Möller and co-workers³⁹ was applied successfully to reproduce the temperature dependence on the surface tension of methane along the orthobaric curve.³⁷ All the parameters used for the modeling of the graphene and methane are listed in Table I. The potential functions used for the flexible graphene are also described in Table I. Nonbonded interactions between graphene and methane are calculated by the Lennard-Jones potential with parameters calculated using the Lorentz-Berthelot mixing rules. The flexibility of the graphene monolayer was also considered through the many-body Tersoff potential.⁴³

TABLE I. Description of the force fields used for the simulation of methane and graphene with the corresponding references.

Parameters and potential functions		
Rigid graphene—Ref. 3		
Cg	$\sigma = 3.3997 \text{ \AA}$	$\epsilon = 0.3594 \text{ kJ mol}^{-1}$
Flexible graphene (FLEX model)—Refs. 3 and 38		
Cg	$\sigma = 3.3997 \text{ \AA}$	$\epsilon = 0.3594 \text{ kJ mol}^{-1}$
Bonding potential— $U(r) = 1/2k_r(r - r_o)^2$		
Cg-Cg	$k_r = 2696 \text{ kJ mol}^{-1} \text{ \AA}^{-2}$	$r_o = 1.42 \text{ \AA}$
Bending potential— $U(\theta) = 1/2k_\theta(\theta - \theta_o)^2$		
Cg-Cg-Cg	$k_\theta = 446 \text{ kJ mol}^{-1} \text{ rad}^{-2}$	$\theta_o = 120^\circ$
Torsion potential— $U(\phi) = k_\phi(1 + \cos(n\phi - \delta))$		
Cg-Cg-Gg-Cg	$k_\phi = 13.17 \text{ kJ mol}^{-1}$ $n = 2$ (multiplicity)	$\delta = 180^\circ$
Methane—united atom model (UA)—Ref. 39		
CH ₄	3.733	1.2464
Methane—all atom model (AA)—Ref. 40		
C	3.500	0.276
H	2.500	0.125

TABLE II. Dimensions of the simulation box (L_x , L_y , L_z) and the number of methane molecules (N). An illustration of different surface areas is provided in Fig. 1.

Surface area ($\text{\AA}^2$)	L_z ($\text{\AA}$)	L_x ($\text{\AA}$)	L_y ($\text{\AA}$)	N	L_x/a	L_y/b
689.6	172.7	27.017	25.524	1 817	3.66	6
1 410.5	221.1	36.841	38.286	4 778	5	9
2 632.9	221.3	51.577	51.048	8 920	7	12
6 550.9	221.0	81.05	80.826	22 194	11	19
10 280.9	220.9	100.698	102.096	34 831	13.66	24

The geometry of the system consists of a graphene membrane located at $z = 0 \text{ \AA}$ surrounded by two methane reservoirs. The z -axis is then perpendicular to the solid-liquid interface. The dimensions of the simulation box are reported in Table II for different system-sizes. MD simulations were carried out with the DL_POLY package (version 4.0)⁴⁴ using the velocity-Verlet algorithm in the Np_NAT ⁴⁵ statistical ensemble where N is the particle number, p_N is the normal pressure to the graphene-methane interface, A is the surface area, and T is the temperature. An anisotropic barostat was used to model the Np_NAT ensemble. The Berendsen thermostat and barostat⁴⁶ with a relaxation time of $\tau_t = 0.5 \text{ ps}$ and $\tau_p = 0.5 \text{ ps}$, respectively, were considered. First, the molecules were randomly inserted in both reservoirs. Second, a phase of equilibration in the canonical ensemble was performed for 5 ns. Third, an equilibration of 10 ns in the Np_NAT ensemble was managed. Eventually, a phase of acquisition was conducted in the Np_NAT statistical ensemble for 10 ns. Periodic boundary conditions were applied in three directions. MD simulations were performed at $T = 120 \text{ K}$ and $p = 1 \text{ bar}$ using a time step of 1 fs. Short range interactions were modeled by using a Lennard-Jones potential with a cutoff radius (r_c) of 12 $\text{\AA}$. Statistical errors were estimated using the block average method.

III. SURFACE TENSION CALCULATION

The surface tension was calculated by using the non-exponential method⁴⁷ based on the test-area methodology³² where γ is expressed as $\gamma = \left(\frac{\partial F}{\partial A}\right)_{N,V,T}$ with F the free energy, A the surface area, N the number of molecules, and V the volume. Let us mention that the non-exponential method was recently developed with a rigorous theoretical background based on the explicit derivation of the partition function.⁴⁷ Thus the non-exponential approach cannot be considered as an approximation of the usual exponential form Test Area (TA). The calculation of $\frac{\partial F}{\partial A}$ was performed by means of an explicit derivation that provides $\gamma = \left(\frac{\partial U}{\partial A}\right)_{N,V,T}$, where U is the configurational energy. This expression was approximated through a finite difference such that $\gamma = \left(\frac{\partial U}{\partial A}\right)_{N,V,T} = \left(\frac{\Delta U}{\Delta A}\right)_{N,V,T}$, where ΔU is the energy difference between two states of different surface areas ($\Delta A = A^1 - A^0$, where 0 stands for the reference state and 1 stands for the perturbed state). To maintain the volume constant, the following anisotropic transformations were used: $L_{x,y}^{(1)} = L_{x,y}^{(0)}\sqrt{1 \pm \xi}$ and $L_z^{(1)} = L_z^{(0)}/(1 \pm \xi)$, where ξ is the perturbation length as $\xi \rightarrow 0$ and L is the

FIG. 1. (a) Illustration of five surface areas of the graphene monolayer. (b) Snapshot of a configuration of the graphene-methane interface where carbon atoms of graphene are in cyan and methane molecules described in the UA model are in pink.

box length. The area of a planar interface is $A = 2L_x L_y$ and $\Delta A = A \left[(1 \pm \xi)^{-1/2} - 1 \right]$. The factor 2 allows us to consider both graphene-liquid interfaces (see Fig. 1). Therefore, the surface tension can be expressed as

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{N,V,T} = \lim_{\xi \rightarrow 0} \left\langle \left(\frac{U^{(1)}(\mathbf{r}^N) - U^{(0)}(\mathbf{r}^N)}{\Delta A} \right) \right\rangle_0, \quad (1)$$

where $U^{(0)}(\mathbf{r}^N)$ and $U^{(1)}(\mathbf{r}^N)$ are the configurational energies of the reference and perturbed states, $\mathbf{r}^N$ and $\mathbf{r}^N$ are the configurational spaces for both states, and $\langle \dots \rangle_0$ stands for the average that is taken over the reference state.

A local version of Eq. (1) can be obtained by assuming the decorrelation of slabs³⁷

$$\gamma(z_k) = \lim_{\xi \rightarrow 0} \left\langle \sum_{i=1}^N \sum_{j>i}^N H(z_{ik}) \left(\frac{u_{zk}^{(1)}(\mathbf{r}_{ij}) - u_{zk}^{(0)}(\mathbf{r}_{ij})}{\Delta A} \right) \right\rangle_0, \quad (2)$$

where k is the index of the planar slab, z_k is the position of the k slab, u_{zk} is the energy of the k th element, $H(z_{ik})$ is the Heaviside function with $H(z_{ik}) = 1$ for $z_i = z_k$ and 0 otherwise, and r_{ij} is the distance between i and j molecules. The surface tension can thus be evaluated as

$$\gamma = \sum_k \gamma(z_k). \quad (3)$$

Let us mention that the exponential route can be approximated by using a development in series⁴⁸ such as

$$\begin{aligned} \gamma &= \frac{k_b T}{\Delta A} \ln \left\langle \exp - \left(\frac{U^{(1)}(\mathbf{r}^N) - U^{(0)}(\mathbf{r}^N)}{k_b T} \right) \right\rangle_0 \\ &= \frac{1}{\Delta A} \left[\langle \Delta U \rangle_0 - \frac{1}{2k_b T} (\langle \Delta U^2 \rangle_0 - \langle \Delta U \rangle_0^2) \right. \\ &\quad \left. + \frac{1}{6(k_b T)^2} (\langle \Delta U^3 \rangle_0 - 3\langle \Delta U^2 \rangle_0 \langle \Delta U \rangle_0 + 2\langle \Delta U \rangle_0^3) \right] \\ &= \gamma_1 + \gamma_2 + \gamma_3, \end{aligned} \quad (4)$$

where $\lim_{\xi \rightarrow 0}$ is removed for clarity.

IV. RESULTS AND DISCUSSION

We report in Fig. 2 the surface tension as a function of L_x for different potential models and cutoffs. A fluctuating surface tension is observed with the UA model and for a cutoff of 12 Å. Indeed, the surface tension decreases from 40 to 80 mN m⁻¹ ($\Delta\gamma = 40$ mN m⁻¹) between $L_x = 27.017$ Å and $L_x = 81.05$ Å. $\Delta\gamma$ corresponds to the difference between the maximum and minimum of the surface tension. This fluctuation is also observed for the liquid-vapour interfaces where an oscillatory surface tension with respect to the surface area has been reported with small variations of $\Delta\gamma \sim 2$ -3 mN m⁻¹.^{49,50} It is the first time that a more strong fluctuation in γ as a function of the surface area is observed. We verified that the so-obtained results are independent of thermostat (Berendsen vs Hoover) and time step ($\Delta t = 1.0$ and 2.0 fs). In addition, the system configuration was also checked by considering a random and pre-equilibrated methane reservoir. On the other hand, it has been shown that the fluctuations of the surface tension of liquid-vapour interfaces can be easily removed from a surface area of 35×35 Å².⁵⁰ As shown in Fig. 2, the size effect on the graphene-methane interface continues on growing beyond $L_x = 36.841$ Å. To check this result, additional simulations were performed for two larger system sizes, $L_x = 201.39$ Å and $L_x = 302.094$ Å. The surface tension was also found fluctuating with these larger systems. Indeed, γ is 64.9 mN m⁻¹ for $L_x = 201.39$ Å, while γ is 76.1 mN m⁻¹ for $L_x = 302.094$ Å. The fluctuating surface tension cannot be thus attributed to the size effects. The surface tension was also calculated from the exponential form given in Eq. (4), and similar results were found. Additionally, γ_2 and γ_3 were also computed [Eq. (4)]. These two last contributions can then be clearly neglected (0.03 mN m⁻¹ for γ_2 and 0.2×10^{-4} for γ_3 in average for all the surface areas), which suggests an absence of an additional entropic contribution.⁴⁸ Recently, it was showed that a possible origin of these fluctuations is the use of a small cutoff.⁵⁰ As suggested in Ref. 50, oscillations can be erased for a large cutoff. Therefore we used a larger cutoff of $L_x/2$ to decrease the dependence on the surface area. Nevertheless, as shown in Fig. 2, the surface tension is always

FIG. 2. Surface tension as a function of L_x at 120 K and 1 bar. UA corresponds to the united atom description while AA is connected to the all atom model.

fluctuating but with a smaller range ($\Delta\gamma = 20 \text{ mN m}^{-1}$) than the range obtained from a cutoff radius of $r_c = 12 \text{ \AA}$ ($\Delta\gamma = 40 \text{ mN m}^{-1}$). Let us mention that the use of the intermediate cutoffs also provides fluctuations in the surface tension. Although the cutoff is not the key-parameter at the origin of this strong fluctuation in γ , its increase from $12 \text{ \AA}$ to $L_x/2$ allowed us to reduce the fluctuation in γ by 50%. Let us mention that the dimension of the box length along the z -direction was also increased from $220 \text{ \AA}$ to $990 \text{ \AA}$ and no effect was observed. Furthermore, MD simulations were also conducted for 150 ns , and no impact of simulation time was evidenced. Eventually, we checked the dependence in the statistical ensemble by carrying out MD simulations (acquisition phase) in the canonical ensemble (NVT). A surface area dependence similar to that obtained in Np_NAT was found that suggests an independence of γ with respect to the statistical ensemble. The impact of the flexibility of graphene on the surface tension was also investigated by using the FLEX and Tersoff models. As shown in Fig. 2, the fluctuations of the surface tension are also established but with a smallest range, $\Delta\gamma = 14 \text{ mN m}^{-1}$, for the FLEX model whereas they have been erased by using the Tersoff model. Indeed, only a size effect is highlighted with the Tersoff potential because the surface tension decreases by 8 mN m^{-1} from $L_x = 27.017 \text{ \AA}$ to $L_x = 51.577 \text{ \AA}$. Recently, Jackson and co-workers have provided the relation allowing the calculation of the entropic (γ_S) and the energetic (γ_E) contributions of the surface tension^{51–53} such that $\gamma = \gamma_E - \gamma_S$ with $\gamma_E = \frac{\langle \Delta U \rangle}{\Delta A} + C$ and $\gamma_S = C$, where C is an additional term of order 2 and 3. Therefore the entropic contribution cannot impact the so-observed fluctuating surface tension.

To unravel the molecular origin of the fluctuating surface tension, density profiles along the z -direction for both $L_x = 27.017 \text{ \AA}$ and $L_x = 81.05 \text{ \AA}$, corresponding to both maximum and minimum in the surface tension, are reported in Fig. 3(a). For the rigid case, Fig. 3(a) shows a layering organization highlighting a strong anchoring of methane on graphene caused by the excluded volume, i.e., the truncation of the solvation shell of methane molecules close to the interface. As depicted in Fig. 3(a), the impact of the graphene on the structure of methane extends over about $30 \text{ \AA}$. Beyond $30 \text{ \AA}$, a flat profile is recovered that corresponds to an absence of correlations between graphene and methane, i.e., the local structure of methane is weakly impacted by the graphene. As exhibited in Fig. 3(a), despite a slight increase in the local density for $L_x = 81.05 \text{ \AA}$, the density profiles of both $L_x = 27.017 \text{ \AA}$

FIG. 4. Two dimensional radial distribution functions between carbon atoms of graphene and methane molecules in the first methane layer close to the graphene surface obtained from the UA model and a cutoff of $12 \text{ \AA}$ for five surface areas at 120 K and 1 bar .

and $L_x = 81.05 \text{ \AA}$ are almost similar. Therefore the difference in the surface tension cannot be imputed to the interfacial density. We report in Fig. 3(b) the local surface tension for both $L_x = 27.017 \text{ \AA}$ and $L_x = 81.05 \text{ \AA}$. The graphene is located at $z = 0 \text{ \AA}$, and as shown in Eq. (2), the contribution at $z = 0 \text{ \AA}$ corresponds to the methane-graphene interactions on the graphene. Figure 3(b) shows that the difference in γ is imputed to the interfacial interactions between graphene and methane. Indeed, the difference in the local surface tension ($\gamma(z)$) at $z = 0 \text{ \AA}$ between both surface areas is about 30 mN m^{-1} , whereas at the positions of the first methane layers the difference in $\gamma(z)$ is around 10 mN m^{-1} . To quantify the interactions between graphene and the first layers of methane molecules, we report in Fig. 4 the two dimensional (2d) radial distribution functions (RDFs) between carbon atoms of graphene and the UA particles of methane close to the interface for five surface areas.

As shown in Fig. 4, several peaks are observed that indicate strong short range correlations between interfacial methane molecules and carbon atoms of graphene. Figure 4 shows that the first peak is around $5.4 \text{ \AA}$ for $L_x = 27.017 \text{ \AA}$ while this distance is shifted toward a lowest value of $4.2 \text{ \AA}$ for $L_x = 36.841 \text{ \AA}$, $51.577 \text{ \AA}$, $81.05 \text{ \AA}$, and $100.698 \text{ \AA}$. This decrease highlights a strengthening of the interactions

FIG. 3. Profiles of density (a) and surface tension (b) of methane described from the UA model along the z -direction at 120 K and 1 bar for both surface areas.

FIG. 5. Two dimensional radial distribution functions between carbon atoms of graphene and methane molecules in the first methane layer close to the graphene surface obtained from the UA model and a cutoff of $L_x/2$ for five surface areas at 120 K and 1 bar.

between graphene and interfacial methane that could explain the increase in the surface tension as a function of the surface area. Interestingly, for $L_x = 100.698$ Å, the amplitude of peaks of RDF strongly decreases that is in line with the decrease in γ for $L_x = 100.698$ Å. We report in Fig. 5 the 2d RDF between carbon atoms of graphene and methane molecules for a cutoff of $L_x/2$. From $L_x = 51.577$ Å, the oscillations were also observed that suggests strong methane-graphene correlations in line with the maximum of the surface tension observed in Fig. 2. Contrarily, no oscillations are evidenced with the flexible graphene that is also in concordance with the small oscillations in the surface tension. The surface tension is therefore strongly correlated to the interfacial methane structure. To investigate this connection, we report in Fig. 6(a) the two dimensional density profile along the x -axis and y -axis directions for $L_x = 36.841$ Å for which the surface tension was increased by 24 mN m^{-1} with respect to that for $L_x = 27.017$ Å.

From $L_x = 36.841$ Å and $r_c = 12$ Å, Fig. 6(a) exhibits a strong anchoring of methane molecules on the graphene surface that is in line with the 2d RDF of Fig. 4. Oppositely, with

FIG. 7. Two dimensional profiles of the density of UA methane and carbon atoms of graphene for $L_x = 100.698$ at 120 K, 1 bar, and $r_c = 12$ Å between $x = -10$ Å and $x = 10$ Å and $y = -10$ Å and $y = 10$ Å. Carbon atom density of graphene corresponds to the green spots.

$L_x = 27.017$ Å and $r_c = 12$ Å, Fig. 6(b) shows a best sampling of the interfacial region from the methane molecules. As observed in Fig. 6(a), methane molecules are located at the centre of benzenic cycles highlighting to a commensurate host-guest organization between both methane and graphene. This possibility to get a commensurable structure is probably the molecular origin of the increase in the surface tension. Indeed, this peculiar organization involves an increase in interactions between graphene and methane leading to an increase in the surface tension. As exhibited in Fig. 6(a), two characteristic distances of the methane network can be evidenced along the x direction, $a = 4.254$ Å and along the y direction, $b = 7.3682$ Å. a and b are reported in Fig. 6(a). If the ratios L_x/a and L_y/b are integers, both graphene and methane networks are then commensurable. As shown in Table II, only three systems present integers along the x and y directions whereas a rational value is found for L_x/a with $L_x = 27.017$ Å and $L_x = 100.698$ Å that is in line with the so-observed surface tension reported in Fig. 2. This absence of the stackability between the host (graphene) and the guest (methane) explains the full sampling of the interfacial region observed in Fig. 6(b) for $L_x = 27.017$ Å. The origin of the fluctuating surface tension and the shape of the 2d RDF are thus connected with the commensurability of both methane and graphene networks.

FIG. 6. Two dimensional profiles of the density of UA methane and carbon atoms of graphene for $L_x = 36.841$ Å (a) and $L_x = 27.017$ Å (b) at 120 K, 1 bar, and $r_c = 12$ Å where red and green colors correspond to the UA methane particles and carbon atoms of graphene, respectively.

TABLE III. Surface tension contributions of UA methane in contact with rigid graphene at 120 K and 1 bar using a cutoff of 12 Å.

L_x (Å)	γ_{tot} (mN m ⁻¹)	γ_{mg} (mN m ⁻¹)	γ_{mm} (mN m ⁻¹)
27.017	43.6	113.2	-69.6
36.841	67.5	106.9	-39.4
51.577	73.0	106.1	-33.1
81.05	87.1	105.2	-18.1

TABLE IV. Surface tension of UA methane in contact with rigid graphene at 120 K and 1 bar using a cutoff of 12 Å with two (2R) and one (1R) reservoirs.

L_x (Å)	γ_{2R} (mN m ⁻¹)	γ_{1R} (mN m ⁻¹)
27.017	43.6	48.7
36.841	67.5	65.7
51.577	73.0	73.6
81.05	87.1	81.7

FIG. 8. Two dimensional radial distribution functions between methane molecules of each first layer of the graphene monolayer described from the UA model and a cutoff of 12 Å at 120 K and 1 bar. An enlargement RDF between 0.9 and 1.05 is provided in the inset.

Despite the rational ratio for $L_x = 100.698$ Å, Fig. 4 shows a strong short range correlation lesser than $L_x = 36.841$ Å, 51.577 Å, and 81.05 Å but higher than $L_x = 27.017$ Å that is in line with the surface tension of Fig. 2. As shown in Fig. 7, that is due to a quasi-commensurable structure where one part of methane molecules and the graphene are commensurable whereas the other molecules are not less anchored on the graphitic surface, leading to an increase in the translational degrees of freedom. That is also at the origin of the decrease in the amplitude of two dimensional RDF for $L_x = 100.698$ Å as reported in Fig. 4. Whereas the increase in the surface tension for higher L_x with respect to the surface tension observed for $L_x = 27.017$ Å was understood in terms of commensurability, the increase of γ from $L_x = 36.841$ Å to $L_x = 81.05$ Å

remains unclear. To unveil it, we decomposed the total surface tension in both methane-methane (γ_{mm}) and methane-graphene (γ_{mg}) contributions. Values of γ_{mm} and γ_{mg} are reported in Table III. From Table III, two facts can be drawn: (i) γ_{mm} provides a negative contribution and ii) whereas γ_{mg} is almost constant as a function of the surface area of graphene γ_{mm} undergoes a drastic increase from -69.6 mN m⁻¹ for $L_x = 27.017$ Å to -18.1 mN m⁻¹ for $L_x = 81.05$ Å. The fluctuations in the surface tension can be then imputed to the methane-methane contribution. Furthermore, the increase in the surface tension cannot be attributed to the interactions of methane molecules in the same layer because the 2d radial distribution functions between methane molecules in the first methane layer are similar to whatever L_x is. The increase in γ from $L_x = 36.841$ Å to $L_x = 81.05$ Å could be thus attributed to the interactions between methane molecules of each side of graphene⁵⁴ separated from a distance of 8 Å. We report in Fig. 8 two dimensional RDF between methane molecules calculated with the UA model located on each side of the graphene monolayer. As shown in Fig. 8, the correlations increase from $L_x = 36.841$ Å to $L_x = 81.05$ Å that is in line with the increase in γ . For the flexible material, the amplitude of surface tension fluctuations drastically decreases because commensurability is prevented due to the displacement of carbon atoms of graphene. Very interestingly, fluctuations disappear with the use of the many-body Tersoff model that allows higher softness and avoid an anchoring of CH₄ molecules on the graphene surface. Eventually, to verify the impact of interactions of methane molecules between both sides of graphene on the surface, molecular simulations were performed with one methane reservoir confined between two graphene walls and two vacuum phases. As exhibited in Table IV, the surface tension is found to fluctuate. This suggests that the origin of this phenomenon is the result of the commensurability.

Interestingly, as shown in Figs. 9(a) and 2, the commensurable organization and surface tension fluctuations can be

FIG. 9. (a) Two dimensional radial distribution functions between carbon atoms of graphene and methane modeled from the OPLS-AA force field ($r_c = 12$ Å) in the first layers of methane close to the graphene surface for four surface areas at 120 K and 1 bar. The RDF is offset by 0.2 units for clarity from $L_x = 36.841$ Å. (b) Profiles of the density of methane described from the AA model along the z -direction at 120 K and 1 bar for both surface areas.

erased by using an atomistic model of CH₄ (OPLS-AA model) preventing all structuration. As exhibited in Fig. 9(a) for the four surface areas, the two dimensional radial distribution functions between graphene and methane are similar, and no structuration is observed that suggests an incommensurable organization. From the OPLS-AA model, the commensurable arrangement between methane and graphene became more difficult to take place given the increase in degrees of freedom of methane. Eventually, we report in Fig. 9(b) the profile of density of methane described by using the AA model along the *z* axis for both L_x. Although the internal interfacial structure drastically differs between UA and AA models, the density profiles are weakly dependent on L_x and on both UA and AA models.

V. CONCLUSIONS

We have reported the surface tension calculation of the graphene-methane solid-liquid interface as a function of the surface area of the graphene monolayer. Two of the most popular UA and OPLS-AA models of methane have been considered. The use of the UA model leads to a strong fluctuating surface tension as a function of the surface area. We have shown that this result is dependent on the cutoff radius. Although the density profiles are similar for all surface areas, profiles of the surface tension are different and underline the fact that the fluctuations in the surface tension are due to the interfacial layers of methane. By calculating the two dimensional density profiles, a connection between the commensurable structure and the increase in the surface tension and its large fluctuations has been established. From a flexible force field to describe and the OPLS-AA force field to model the methane, the commensurable organization is erased and fluctuations of the surface tension as a function of the surface area are significantly reduced and become of the same order of magnitude as those obtained with the liquid-vapor interfaces. The reduction of fluctuations is then due to an increase in the translational degree of freedom of atoms preventing the host-guest commensurability. This work shows that the using of two simple models (UA and rigid force fields) can lead to an unphysical structure and fluctuating surface tension. Eventually, although the model is clearly at the origin of the large surface tension fluctuation, size effect and long range corrections have to be considered to get a quantitative surface tension.

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